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Qualitative Analysis

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An Introduction
to the
Theory and Practice of Qualitative
Analysis by Solution

BY
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¹⁾
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GENERAL

This book is dedicated with the highest esteem
to
Edward F. Bartholomew and Wilhelm Ostwald
my first and last masters in science.

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P R E F A C E

The study of Qualitative Analysis has latterly fallen somewhat into disrepute in American colleges. I believe that the reason for this is three-fold: 1st. The empirical treatment given the subject until recently in lectures and texts, resulting in the latter instance in such remarkable complication that I have never yet seen an undergraduate who could read one without assistance. 2nd. The queer compositions, called *Unknowns*, that are generally given students for practice. Casuistically speaking, these mixtures might be worshipped—as it may be safely assumed that some do—inasmuch as they are not the likeness of anything that is. 3rd. The fact that the teaching of this branch of Chemistry is frequently committed to the hands of young instructors whose knowledge and pedagogic skill are not always adequate to the demands, often great, made upon them.

A score of years' experience convinces me that Qualitative Analysis may be made to yield discipline of a high order; its utility as a tool in the prosecution of chemical investigations is admitted by nearly every one. I have therefore prepared this little book in the hope that I might, through it, be able to somewhat promote study of this subject. I do not claim that this treatise is so plain that a wayfarer, though a Freshman, need not err therein, nor that it will either dispense with the instructor or make his post a sinecure. However, I have sincerely endeavored to render the plan simple, the philosophy scientific, and the scheme of analysis so obvious that students of average abilities will be able to acquire from the book a creditable knowledge of the subject; as for the others—*gegen die Dummheit selbst die Götter kämpfen vergebens*. There will always be a field for the instructor. Indeed, he is the one indispensable feature of a laboratory. While the methods employed are drawn from the classic of Fresenius, the explanations are derived from the modern theory of solutions; and I have sought to render every step of the way continuously rational to the learner by means of cross references.

I wish to record here my conviction that Qualitative Analysis, in whatever state of dilution, is not adapted to the curriculum of secondary schools. The study is too abstruse for immature students. As a rule, they can at best only learn to make a set of test-tube manipulations by rule-of-thumb. If they proceed to college, this experience will often be found encysted as a wen of conceit which must be cut out before healthy, intellectual growth can take place. Possibly herein may be found a fourth reason why this branch of Chemistry has suffered declension in the esteem of college teachers.

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Qualitative Analytical Chemistry

CHAPTER I

INTRODUCTION

1. Chemistry defined.—Chemistry is that branch of science which treats of those properties of bodies which are functions of their composition and constitution. That division of the subject which teaches how to ascertain the composition of bodies is called Analytical Chemistry. By analysis we may find what elements are present in a compound, and also the relative amount of each. The first of these processes is called qualitative; the second, quantitative.

2. Definition of Qualitative Analysis.—Qualitative Analysis is, consequently, that branch of Analytical Chemistry which is devoted to methods for finding what chemical elements (and, sometimes, radicals, or compounds) are present in a body. This definition is comprehensive. The present treatise will be restricted to a study of the more abundant elements and their common compounds, chiefly inorganic, as they are likely to be found in nature and in the products of manufacture.

3. The identification of substances.—Chemical analysis is both a science and an art. We identify material things by means of characteristic trains of sense impressions. The simplest case of recognition is amazingly complex. The human infant requires months of association under constant instruction to enable it to detach its own species from the universe and isolate itself as a conscious unit. If the child be given at this stage a lump of loaf sugar and told at the same moment the word sugar, it

receives through the eye an impression of color; through the hand, the ideas of hardness and weight; through the eye and the hand conjointly, the percepts of form and dimension; and, finally, the organs of taste and digestion add those sensations of sweetness and satisfaction which complete the concept *sugar*. A repetition of the process at intervals during a few weeks establishes a train of nerve-cell adjustments whose recognition by the percipient is called memory; and thereafter this entire series of cell adjustments may be produced by a renewal of but one or two of the original sensations, the remainder being automatically interpolated. After a short time the child is able to identify sugar quickly and positively. From this experience as a point of departure, it proceeds in like manner to differentiate the generic, sugar, into the specific varieties—loaf sugar, granulated sugar, molasses, etc. And its acquaintance with the world at large is gradually extended by the same empirical process.

If later the child, now a youth, undertakes the study of Chemistry, he will familiarize himself with elements and compounds by precisely the same method. Expertness in differentiating and classifying such substances is dependent, primarily, upon the delicacy of adjustment of the nervous system, that is, upon talent; and, secondarily, upon practice. In so far, chemical analysis is an art. But the task of the chemist, which is no less than to acquire a positive acquaintance with the ultimate composition and characteristic qualities of every accessible body in the material universe, is greatly abridged and lightened by the classification of phenomena, substances, and bodies by certain principles which render the world rational to us, and which we name *natural laws*. In this aspect, chemical analysis is a science.

4. Precautions to be observed.—For the reasons adduced, the student should not expect immediate and invariable success in his laboratory determinations. Expertness comes only from long and intelligent practice. Moreover, no process of analysis is perfect, because nothing of human invention is perfect. Consequently, it is necessary for the student to exercise scrupulous cleanliness and rigorous care in carrying out directions, and to have thorough knowledge of what he is about.

CHAPTER II

THEORY OF SOLUTIONS

5. The identification of a substance necessitates its being carried through a series of transformations (§ 3) whereby the individual components are made, at the will of the experimenter, to assume new combinations, in which, one of the components being known, the other is recognized by the specific properties of the whole newly-formed compound. Such transformations are generally effected most readily in aqueous solutions.

6. Solution defined.—The substantive, *solution*, signifies a mixture whose components are in equilibrium and incapable of being completely separated by ordinary mechanical processes. The substance in which solution takes place is called *the solvent*; the substance which is dissolved is called *the solute*. Solution may occur either with or without metathesis. In the present chapter, only the latter kind of solution will be discussed.

A solute is said to be dissolved in a solvent when it becomes molecularly diffused throughout it. The solute may be uniformly distributed throughout the solvent so as to form a homogeneous mixture; but, as a rule, this is not the case when an interval of time has elapsed after thorough agitation.

No solvent is known that is not to some extent soluble in its solute; therefore, in speaking of solutions it is necessary to specify which is taken as solvent and which as solute. This may be done by placing the name of the solvent after the preposition *in*, thus—"Dissolve alcohol in water."

7. Kinds of solution.—Different kinds of solution may occur. We may have a solution—(1) of a gas *in a gas*; (2) of a gas *in a liquid*; (3) of a gas *in a solid*; (4) of a liquid *in a gas*; (5) of a liquid *in a liquid*; (6) of a liquid *in a solid*; (7) of a solid *in a gas*; (8) of a solid *in a liquid*; (9) of a solid *in a solid*.

(1) The solution of one gas in another is illustrated by the diffusion of atmospheric oxygen in nitrogen. In practice, this kind of solution is usually effected by introducing the solute into the solvent retained in a flask or bottle by means of a water or a mercury bath. The solute penetrates the solvent till uniform admixture results. The properties of the mixture are the sum of the properties of the constituents. Hence, the expression of the simple-gas law, $PV=RT$, transformed for a gas-solution becomes $PV=p_1v_1+p_2v_2+p_3v_3+\dots=RT$. This is Dalton's law.

(2) The solution of a gas in a liquid is illustrated by hydrogen sulphide in water. This kind of solution is best accomplished by passing the gas into the fluid by means of a delivery tube and causing minute bubbles to ascend through the greatest depth of solvent obtainable under the circumstances. Obviously the operation will be accelerated by keeping the solvent in motion. The amount of gas that will be absorbed depends primarily upon the nature of the gas and of the liquid, different liquids absorbing different amounts of the same gas, and secondarily upon pressure and temperature, being a direct function of the pressure and an inverse function of the temperature. This is Henry's law. Mixed gases are absorbed directly in proportion to their partial pressures in accordance with Dalton's law.

(3) The solution of a gas in a solid is illustrated by hydrogen in palladium. Since it has been shown that gases dissolve in any solvent in the direct ratio of their pressure, this variety of solution also obeys the laws of Henry and Dalton.

(4) The solution of a liquid in a gas is illustrated by the absorption of water in air. This kind of solution is accomplished by allowing the liquid to stand some time in a suitable vessel containing the gas or by passing a stream of gas through the liquid. Dalton discovered that a liquid in the presence of a gas exerts the same vapor-pressure as when in a vacuum; hence this kind of solution proceeds to saturation in direct ratio to the temperature.

(5) The solution of a liquid in a liquid is illustrated by alcohol in water. This kind of solution is practically accomplished by pouring

the solute into the solvent and stirring or shaking the mixture. Two cases are involved: (a) solute and solvent mix in all proportions; (b) the liquids are only partially miscible. Physically, the properties of a mixture belonging to class (a), unlike the corresponding class of gas-solutions, are not the sum of the properties of the constituents. Thus, the volume of the mixture, V , is never equal to the sum of the volumes of the constituents, $v_1 + v_2, \dots$, but is either less or greater. Class (b) is physically still more complex; but since at some elevated point of temperature solutions of class (b) pass over into class (a), the former may be regarded as a variety of the latter.

(6) The solution of a liquid in a solid is illustrated by mercury in zinc. It appears from the studies of van't Hoff that such solution is governed by the same laws as that of liquids in liquids.

(7) The non-metathetical solution of solids in gases is called *sublimation*. The vaporization of iodine in air illustrates this variety of solution. The sublimation pressure varies directly with the temperature up to the melting point of the solid. The properties of such a solution are the sum of those of its constituents.

(8) The solution of a solid in a liquid is illustrated by sodium chloride or cane sugar in water. In practice, such solution is facilitated by pulverizing the solid and adding it to the solvent with stirring or shaking. The operation is helped by heating the solvent if endothermy takes place and by cooling it if exothermy occurs. In this kind of solution, the influence of pressure is that of an inverse function; but since all qualitative operations are carried on at atmospheric pressure, this agency may be neglected.

(9) The solution of a solid in a solid is illustrated by the penetration of carbon into iron as formerly practiced in making steel by heating charcoal and iron in earthenware boxes, and by the fact that if a piece of zinc be electroplated on one side with copper the zinc gradually penetrates the copper and whitens it. This variety of solution appears to follow the same laws as does the solution of a liquid in a liquid.

8. Saturation.—When a solvent contains all the solute that it can dissolve at a given temperature and pressure it is said to be saturated. Variation in either temperature or pressure will produce in such a solution either a deposition or a further absorption of the solute, as explained above. However, the condition of saturation does not invariably follow instantly changes in the conditions under discussion. Thus, a saturated solution whose temperature is lowered or pressure reduced may only deposit its excess of solute after an appreciable interval. Nevertheless, the equilibrium of the mixture is rendered at once unstable, and it will finally pass to a state of stable equilibrium corresponding to the new conditions. When such change of conditions would theoretically necessitate a separation of solute *that does not occur*, the solution is said to be supersaturated.

9. Solubility.—The solubility of a substance is the number of grams thereof which 100 grams of the solvent can dissolve at a given temperature under the pressure of one atmosphere.

10. Osmosis.—If an aqueous solution be covered by a layer of pure water, the solute begins at once to diffuse into it; and this operation continues until the mixture becomes homogeneous throughout the entire mass. However, the migration of the solute may be arrested by interposing between the two portions of the solvent a wall that is permeable by the solvent but not by the solute. Such partitions are called *semipermeable*. They may be made of certain animal or vegetable tissues, or layers of amorphous chemical compounds, as ferrocyanide of copper, laid down by chemical reaction in earthenware cells. When such a cell, fitted with a manometer, is filled with a solution and placed in pure water, the latter begins at once to pass into the cell. Since none of the solute can escape from the cell, the pressure therein is increased and registered by the manometer. If the temperature be kept constant, the operation goes forward to a maximum which is directly proportional to the strength of the solution. The ingress of water can be hindered by exerting a pressure upon the solution in the cell in the opposite direction. When such pressure becomes equal to that exerted by the water passing into the cell, mi-

gration of water ceases. The force exerted to accomplish this, it will readily be seen, is capable of being exactly measured; it is an equivalent of the counter pressure of the solution, and its value is called *the osmotic pressure* of the solution. In practice, the value of the osmotic pressure is instantly determined by taking the maximum reading of the manometer.

It thus appears that a substance in solution behaves as though it were in the gaseous state. For, by Boyle's law, the pressure exerted by a gas is proportional to the volume, i. e., the concentration. Hence the gas equation, $pV=RT$, *applies to all solutions*. The osmotic pressure is, therefore, proportional to the mass of the solute and always the same for a given solvent; but its value varies with different solvents. Hence, the gas equation generalized for solutions becomes $pV=iRT$, i being a constant factor for the solvent employed and p being the osmotic pressure.

II. Vapor pressure.—It is a familiar fact that a liquid exposed to the air will continuously give off vapor till the whole has evaporated. If, however, the liquid be in a stoppered bottle, evaporation will go steadily forward, at constant temperature, till the contained air is saturated. At this point, the pressure of the vapor upon the internal walls of the bottle, including of course the free surface of the liquid, is equal to the force operating between the particles of the liquid tending to drive them through the surface of the fluid. The former force is called *vapor pressure*; the latter, *vapor tension*.

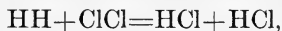
The vapor pressure of a liquid may be measured at different temperatures with a manometer. Since at the boiling point vapor pressure and tension are equal, we may measure variations in tension by noting variations in boiling point at the constant pressure of the atmosphere.

Now the vapor tension of a solvent is lowered by the introduction of a solute, so that the boiling point of a solution is always higher than that of the pure solvent; or, conversely, the freezing point of a solution is lower than that of the pure solvent. The lowering of the vapor tension has been found to be *in proportion to the mass of solute present*.

Hence, it appears that evaporation is a variety of osmosis in which the free surface of the liquid plays the role of a semipermeable membrane; it is permeable for the solvent but not for the solute.

If we now substitute *equimolecular masses* for *equal masses* where the latter words occur in the foregoing discussion, it appears that *the lowering of vapor tension (decrease of osmotic pressure) in a given solvent produced by the solution of gram-molecular weights * of different solutes is a constant*. This fact is utilized in the determination of molecular weights by the well known equation $M = c \frac{s}{\Delta L}$, where M is the molecular weight of the dissolved substance, s its weight in grams, Δ is the observed elevation of the boiling point (or depression of the freezing point), L is the weight in grams of the solvent used, and c is the constant for molecular depression depending upon the particular solvent employed. But the discussion is introduced here in order to lay a foundation for the matter presented in the next section.

12. Ionization.—Several classes of compound substances when dissolved in water (and in a few instances in certain other solvents) do not conform to the rule enunciated in the last paragraph. Their molecular weights, determined from aqueous solutions by the boiling point and freezing point methods, are approximately small multiples (2-5) of what they should be. From the fact that hydrochloric acid gas is made from its constituent gaseous elements reacting *by volume*, thus—



and the weights of the reacting volumes being respectively 2 and 71, we conclude that the molecular weight of HCl is 36.5. But the depression of vapor tension in an aqueous solution of HCl yields a value for the constant c , (almost) twice as great as it should be to correspond with the accepted molecular weight. Assuming that the solution law (§ 11) holds good in this case, the only possible explanation of the phenomenon is the dissociation of the molecules of the solute,

*A gram-molecule, or mol, of a substance is its molecular weight in grams; e. g., a gram-molecule of NaCl is 58.5 grams. In practice, we may employ a convenient fractional part of this.

one molecule of hydrochloric acid yielding two new *sub-molecules*, one of hydrogen and one of chlorine. The correctness of this assumption is shown by the fact that all solutions which manifest an abnormal lowering of vapor tension are conductors of the electric current while other solutions and pure water are not.

Substances whose aqueous solutions conduct the electric current are comprised in the three familiar classes of chemical compounds—acids, bases, salts. They are called, comprehensively, *electrolytes*. If the electrodes of a voltaic cell, or other source of the electric stream, be introduced into the solution of an electrolyte, its hydrogen or metal is separated and deposited on the cathode, and simultaneously the non-metal or non-metallic radical appears at the anode. The explanation of this behavior can be found only in the fact that *opposite kinds of electricity attract*. Now, the anode (the electrode from which the current travels) is charged with positive electricity, and the cathode (the electrode to which the current flows) is charged with negative electricity. Hence, we conclude that dissociated hydrogen and metal atoms and metallic radicals are charged with positive electricity, and that not-metal atoms and non-metallic radicals are charged with negative electricity. The particles that migrate under influence of the electric current are called *ions*. Ions that carry charges of positive electricity are called positive ions or cations; those that carry charges of negative electricity are called negative ions or anions. Since pure water does not conduct the current, it is obvious that ionization in solutions is caused by the water only. This is called *electrolytic dissociation* or *ionization*. The separation of ions from solutions by means of the electric stream is called *electrolysis*. Since electrolysis establishes the fact that molecules of electrolytes are dissociated by solution into two or more independent parts, we have in the existence of ions the explanation of the abnormal vapor tension exhibited by such compounds.

13. Classes of electrolytes defined.—An ion differs from an ordinary atom or radical in that it is a free particle and has associated with it a charge of electricity. Hence, the symbol for an ion is written

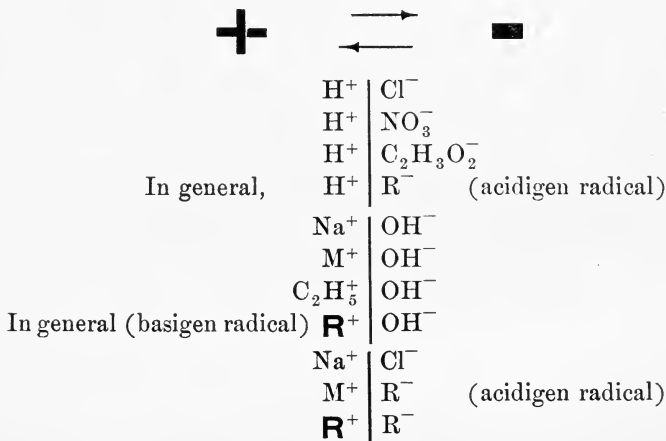
with electricity symbols added, thus— H^+ , Na^+ , Ca^{++} ; Cl^- , O^{--} , NO_3^- . The valence of an ion is indicated in its symbol by the number of electricity charges. Since in aqueous solution, acids dissociate into H^+ and a not-metal radical, and bases dissociate into OH^- and a metal radical, and salts dissociate into a metal radical, M^+ , and a not-metal radical, non- M^- , we may define these classes of electrolytes as follows:

An acid is a compound whose water solution contains free hydrogen ions.

A base is a compound whose water solution contains free hydroxyl ions.

A salt is a compound whose water-solution contains free metal or metallic-radical ions and free not-metal or not-metallic-radical ions. Or, more briefly, *a salt* is a compound whose water solution contains both basigen and acidigen ions.

These definitions are illustrated in the subjoined diagram.



14. Degree of dissociation.—Inasmuch as the ionization of an electrolyte is caused by the process of solution (§ 12), it follows that the degree of ionization varies directly as the dilution; and at infinite

dilution, it becomes infinitely great. The degree in a given case may be ascertained by measuring the electric conductivity of the solution according to methods given in treatises on Physics. It has thus been ascertained that equivalent solutions* of most of the ordinary electrolytes are practically completely dissociated upon reaching a thousand-fold dilution. Exactly defined, the degree of dissociation (α) of a dissolved electrolyte at any stage of dilution is equal to the ratio of molecular conductivity at this stage (μ) to the molecular conductivity at infinite dilution (μ_{∞}), or

$$\alpha = \frac{\mu}{\mu_{\infty}}$$

15. Modes of ionization.—Molecules of electrolytes break down into an *equivalency* of cations and anions—thus $\text{HCl} = \text{H}^+ + \text{Cl}^-$, $\text{KOH} = \text{K}^+ + \text{OH}^-$, $\text{Ca}(\text{OH})_2 = \text{Ca}^{++} + \text{OH}^- + \text{OH}^-$, etc. Other modes will be discussed later (§ 20).

16. Physical solution.—The kinds of solution discussed in this chapter are commonly termed *physical*. Physical solution, it will be remarked, embraces the solution of electrolytes and non-electrolytes in all cases not accompanied by metathesis.

*Equivalent solutions are those containing in equal volumes those weights of reagents which react with one another upon a hydrogen basis, e. g., 40g. Na OH=36.5g. HCl=49g. H_2SO_4 . They are made by dissolving the calculated weight of reagent in 1000 cc. of water.

CHAPTER III

THEORY OF SOLUTIONS CONTINUED

METATHESIS

17. Solvents.—The solvents generally used in analysis are water, the alkali hydroxides and sulphides, the common acids, carbon bisulphide, ether, and ethyl (or methyl) alcohol. The solution effected by water is usually physical; but it may be accompanied by chemical change as seen in the solution of alkali oxides. Alcohol, ether, and carbon bisulphide are used to but a very limited extent in qualitative work, and chiefly as physical solvents. Consequently, the most important chemical solvents are aqueous solutions of the common acids and alkalis.

18. Chemical activity.—It has been ascertained by experiment that substances, even those with which we associate the idea of the highest chemical activity, are incapable of reaction except in the presence of some agent capable of producing dissociation. Thus, dry chlorine does not react with fused sodium, and dry phosphorus does not burn in dry oxygen. Water is the most powerful dissociating fluid known. Since electrolytes manifest their greatest activity in very dilute solutions, wherein we may assume dissociation to be complete (§ 14), it is obvious that chemical activity, or *strength*, depends upon degree of ionization, and *chemical reaction occurs between the ions*.

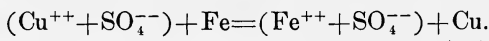
In equivalent, or *normal*, solution (§ 14), it is shown by the measurement of their electric conductivities that *neutral salts* are dissociated to the extent of 80 or 90 *per cent*; the *strong acids*—HCl, HBr, HI, HNO₃, H₂SO₄, HClO₃, HClO₄, and the thionic acids, to about the same extent; the *moderately strong acids*—H₃PO₄, H₂SO₃, HC₂H₃O₂, to less than 10 *per cent*; and the *weak acids*—H₂CO₃, H₂S, HCN, H₃BO₃, H₂SiO₃, to less than 1 *per cent*; the *strong bases*—hydroxides of the alkali and the alkaline-earth metals, to 80 or 90 *per*

cent; the *moderately strong bases* — NH_4OH , $\text{Mg}(\text{OH})_2$, Ag_2O (AgOH does not occur free), to less than 10 *per cent*; hydroxides of other metals are *weak bases*, dissociating to less than 1 *per cent*.

19. Chemical reactions.—It appears from the discussion given in the preceding section that chemical reaction only takes place between ions. How this occurs may be illustrated by the familiar experiment of making common salt, NaCl . The solution of sodium hydroxide is electrolytically dissociated into Na^+ and OH^- . The solution of hydrochloric acid is dissociated into H^+ and Cl^- . This admits of readjustment according to the law of electrical attraction by which the Na and Cl ions on one hand and the H and OH ions on the other are brought together, and molecules of NaCl and H_2O result. Since sodium and hydrogen ions are both electro-positive, it might seem that each has fully as good a chance to reunite with its own anion as with that of the other, unless *ionic attractions are of different values*; but we know this to be the case, as otherwise chemical readjustment could never take place.

20. Metathetical ionization.—Ionization may occur otherwise than by electrolytic dissociation. There are three cases which may be illustrated by the following familiar facts:—

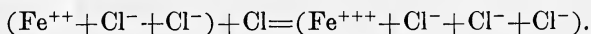
1. If an iron spatula be dipped into a solution of copper sulphate, iron goes into solution and copper is deposited,—



2. A piece of gold-leaf readily dissolves in chlorine-water,—



3. A substance in solution may have its degree of valence altered, as when ferrous chloride is changed to ferric chloride by treating it with nascent chlorine,—



Reactions may be met with which fall entirely within the purview of one of the four modes of ionization (§§ 12, 15; and the preceding paragraph of this section); others may demand two or more for their full elucidation.

21. Chemical equilibrium.—The statement concerning chemical reaction given in section 19 does not present all of the facts involved. It is therein assumed, first, that the solute, sodium hydroxide, is in its solvent, water, wholly ionized— $\text{NaOH} \rightleftharpoons \text{Na}^+, \text{OH}^-$; second; that the solute, hydrochloric acid, is in its solvent, water, also wholly ionized— $\text{HCl} \rightleftharpoons \text{H}^+, \text{Cl}^-$; and, third, that the products of metathesis, common salt and water, are in the common solvent, water, entirely undissociated:—

1. $\text{Na}^+ + \text{OH}^- + \text{H}^+ + \text{Cl}^- \rightleftharpoons [\text{NaCl}] + [\text{H}_2\text{O}]$. The first two assumptions might be actually attained (§14); but the third assumption can not be attained in practice (§§15, 18). Hence, for purposes of general illustration, equation 1 must be replaced by the following form:—

2. $x[\text{NaOH}]^* + y\text{Na}^+ + y\text{OH}^- + w[\text{HCl}] + z\text{H}^+ + z\text{Cl}^- \rightleftharpoons v[\text{NaCl}] + v[\text{H}_2\text{O}] + t\text{Na}^+ + t\text{Cl}^- + s\text{H}^+ + s\text{OH}^-$. This equation indicates the facts, namely, that in a solution containing caustic soda and hydrochloric acid some molecules of the reagents ionize, these ions interact to produce some molecules of sodium chloride and water, certain molecules whereof are further electrolyzed into their original ions. In other words, the reaction is *incomplete* and to some extent *reversible*. So that equation 2 may be written yet more concisely thus,—

3. $[\text{NaOH}] + \text{Na}^+ + \text{OH}^- + [\text{HCl}] + \text{H}^+ + \text{Cl}^- \rightleftharpoons [\text{NaCl}] + [\text{H}_2\text{O}] + \text{Na}^+ + \text{Cl}^- + \text{H}^+ + \text{OH}^-$. It will be noted that equation 3 represents two reactions, the first proceeding from left to right and the second from right to left. *These reactions are not occurring alternately without termination*, else no reaction could be carried to a definite stage of completion. Instead, the reaction towards the right hand begins at a maximum rate and gradually diminishes in velocity, while simultaneously the reaction towards the left hand begins at zero and increases in velocity until NaCl is produced at precisely the same rate at which it is being ionized. When this condition is attained, *chemi-*

*A formula thus bracketed indicates an undissociated molecule.

cal equilibrium results, and no further change can occur in the solution so long as temperature and pressure are constant.

22. Rate of reaction.—The speed of reaction is expressed by the law of mass action as follows: *When substances react chemically with one another the rate of action is in direct ratio to the active masses of the reagents.* By “active mass,” we understand concentration of ionic mass (§ 18 and § 23).

23. Concentration of a solution.—The distribution of a reagent in its solvent is in accordance with the physical laws previously set forth (§§ 7, 14, 15). The number of gram-molecules* of a given solute present in 1000 cc. of solvent is called *the concentration*. In a saturated solution (§ 8) in the presence of some undissolved solute, there is a state of equilibrium between the dissolved and undissolved portions of the solute, and also between the dissociated and the undissociated portions of the solute in solution. Thus, in the case of sodium hydroxide, we have the equilibrium equation $[\text{Na}^+] \times [\text{OH}^-] = c^\dagger [\text{NaOH}]$, wherein the bracketed formulas represent the respective concentrations. But for a given solvent, the portion undissociated is of constant value; therefore, the product of the left-hand members of the equation is constant, which is to say that *in a saturated solution the product of the ion-concentrations is always of the same value*. The product obtained by multiplying together the values of the ion-concentrations is called *the solubility-product*.

Since the concentration of the ions is readily measured (§ 14), we may easily ascertain what relationship subsists between the solubility of a substance (§ 9) and this factor. Experiment shows that *solubility is a direct function of the solubility-product*.

If the equilibrium equation for sodium hydroxide be written with concentration-factor symbols, it takes the form $k_2 k_3 = k_1$, which is perfectly general for all electrolytes of the same class. Experiment

*See § 11, foot-note.

†This c is the constant of dissociation for the given solvent. See § 11, last paragraph, and § 12, first paragraph.

shows that over a wide range of dilution the quotient of $k_2 k_3 \div k_1$ is practically constant in value, or

$$\frac{k_2 k_3}{k_1} = C.$$

This may be read — The product of the ion-concentrations is directly proportional to the concentration of the undissociated solute. But this is only the law of mass-action in other words. The above mathematical formulization of the law is found convenient in discussing reactions.

24. Change of equilibrium.—It is obvious on inspection of the above equation that a change in one of the factors of a reaction destroys the equilibrium then existing, and necessitates a corresponding change in the other factors before a new state of equilibrium can ensue. Two cases may arise:—

a. The concentration of one of the ions is increased in a saturated solution. Since the value of the product, $k_2 k_3$, cannot increase, an increase of one kind of ion must be accompanied by corresponding decrease of the other whereby k_1 is produced and precipitated. To illustrate: Let sodium chloride be the solute in question. The equilibrium equation for its saturated solution is $\text{Na}^+ \times \text{Cl}^- = c [\text{NaCl}]$. If now the chlorine ions be increased in any way, as by adding to the solution HCl, or KCl, or chlorine gas, etc., the solubility-product is exceeded, rendering the quotient, $\frac{k_2 k_3}{k_1} = C + x$, too large for equilibrium, and necessitating the deposition of the excess, x . It therefore appears that *the solubility of an electrolyte is decreased by the presence of another with which it has an ion in common.* For this reason we use in practice “an excess” of the reagent.

b. The concentration of one of the ions is diminished in saturated solution. If the concentration of either kind of ion be lessened, as by taking up a simple ion to form a more complex ion (§ 20) or an undissociated molecule, the value of the quotient in the equilibrium equation becomes too small by x , necessitating more of the solid solute dissolving and ionizing in order to restore equilibrium. Wherefore,

the solubility of an electrolyte is increased by decreasing the concentration of one of its ions. Illustrations: (1). A slightly dissociated base (§ 18) dissolves more readily in acid than in water solution. From the fact that water is a non-conductor of the electric current (§ 12) it follows that it ionizes ($\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$) to but an infinitesimal extent. Therefore when a strongly ionized acid, as HCl , and a slightly ionized base, as $\text{Mg}(\text{OH})_2$, are brought together the H^+ of the acid at once unites with the OH^- of the base, forming undissociated H_2O . This diminishes the value of the solubility-product-factor OH^- , necessitating more of the solid solute, $\text{Mg}(\text{OH})_2$, dissolving. (2). The salt of a *weak** acid dissolves in a *stronger* acid. Thus, $\text{NaC}_2\text{H}_3\text{O}_2$ dissolves in HCl . Here, the $\text{C}_2\text{H}_3\text{O}_2^-$ ion unites with the H^+ of the acid, producing slightly dissociated $\text{HC}_2\text{H}_3\text{O}_2$. (3). The formation of a complex ion by the metathesis facilitates solution. Thus, ferrous hydroxide, which is but slightly soluble (Fe^{++} , OH^- , OH^-), dissolves readily in potassium cyanide (K^+ , CN^-) because the latter anion reacts with Fe^{++} to form the complex ion $\text{Fe}(\text{CN})_6^{--}$. (4) The formation of an undissociated molecule facilitates solution. Thus, lead hydroxide, which is but slightly soluble in water, readily dissolves in sulphuric acid. Here, the SO_4^{--} unites with the Pb^{++} , forming undissociated PbSO_4 which is precipitated and so removed from participation in the reaction, thereby necessitating a continuous production of OH^- in the attempt to maintain an equilibrium.

Since the chemical activity of an electrolyte is in direct proportion to the degree of ionization (§§ 18, 22), it follows as a corollary to *proposition a* that *weak acids and bases are rendered yet weaker by the presence of their neutral salts.* This is taken advantage of in order to expel a volatile product of reaction by heat, or to render it *inactive* in the presence of other reagents. Thus, a solution of ammonium hydroxide is but slightly dissociated into NH_4^+ , OH^- . If now a strong base, as NaOH , be added, the increase of OH^- ions necessitates the formation of undissociated NH_4OH , which, being volatile, is

*See § 18.

readily driven from the solution by heat. Again, the addition of NH_4Cl (NH_4^+ , Cl^-) to a solution of MgCl (Mg^{++} , Cl^- , Cl^-) causes a regression of the latter ions into undissociated MgCl_2 and so prevents the precipitation of MgCO_3 by NH_4CO_3 .

25. Hydrolysis.—The action of water whereby solutions of certain neutral salts show “an acid” or “an alkaline reaction” is called hydrolysis. For example, Na_2CO_3 reacts alkaline, and SnCl_2 reacts acid. This is due to the regression of ions into undissociated molecules (§ 24, b, 4). In the solution of sodium carbonate, we have the ion-factors Na^+ , Na^+ , CO_3^{--} ; H^+ , OH^- . The products are H_2CO_3 , but slightly ionized, and NaOH , strongly ionized (§ 19), consequently an alkaline reaction. In the stannous chloride solution, we have the ion-factors Sn^{++} , Cl^- , Cl^- ; H^+ , OH^- . The products are $\text{Sn}(\text{OH})_2$, very slightly ionized, and HCl , very strongly ionized; hence, an acid reaction. In the case of some metalloids, as tin, the regression into undissociated molecules may go so far as to lead to their precipitation in water solution as hydroxides and basic salts.

26. Completion of reactions.—It appears (§ 21) that all reactions are to some extent reversible. However, for analytical purposes, we select those that may be rendered *practically* complete under easily attainable conditions. This may lead us to the precipitation of a salt, the formation of a soluble complex (either molecular or ionic) with a markedly individual color, or to the formation of undissociated volatile molecules of characteristic odor.

Before a substance can be precipitated, the solution must be rendered saturated with its undissociated molecules (§ 24, a). By way of illustration, we will now complete the discussion of the reaction by which we obtain sodium chloride (§§ 19, 21). Chemical equilibrium having been established, we have to saturate the solution for $[\text{NaCl}]$. While this may be done by the methods indicated in § 24, a, in practice we resort to another method for increasing the concentration of the $[\text{NaCl}]$, namely, removal of the other association product, $[\text{H}_2\text{O}]$. This is done by evaporation. The operation, therefore, transpires thus: By solution, there results $[\text{NaOH}]$, Na^+ ,

OH^- , $[\text{HCl}]$, H^+ , Cl^- ; some ions react, forming $[\text{NaCl}]$ and $[\text{H}_2\text{O}]$, necessitating further ionization of the reagents to restore the equilibrium thereby lost; and so proceeding towards saturation. The experimenter meanwhile hastens the outcome by evaporating some $[\text{H}_2\text{O}]$, thereby reducing the ionizing power of the solvent-mass and consequently increasing the relative number of undissociated molecules of sodium chloride. The chemical process of reaction and the physical process of evaporation, proceeding from opposite directions, thus converge along lines which meet at the saturation-point. The moment this is passed *some precipitation occurs*. Finally, the reagents having been completely ionized, and no more water being present to occasion reverse ionization of NaCl , nothing but the latter substance remains.

The evaporation method for effecting precipitation is not much used in qualitative work. Obviously that result is more expeditiously reached by producing metathetically a new molecule whose solubility-product is slight (as PbSO_4 , § 24, *b*, 4). But in reactions whereby one product may eventuate as a solid and the other as a liquid (as in the case of NaCl), the method is well adapted to securing all of the solid product. It is also utilized in separating solid-solutes having differing solubility products. The latter operation is called *fractional crystallization*.

CHAPTER IV

THE ANALYTIC GROUPS

27. The course outlined.—The number of bodies is infinitely great, and an infinity of time would be required by an intelligent being merely to pass them in review. And were our knowledge of them derived solely from their particular properties, an eternity would be needed in order to acquire “a working knowledge” of the world about us. Fortunately, we have a more expeditious way for acquiring such information (§ 3, last paragraph). The student is already aware from the study of General Chemistry that all aggregates of matter fall into two classes*—*simple bodies* (elements), and *compounds* (combinations of two or more elements); and that compounds are naturally divided into *binaries* (as oxides, sulphides, nitrides, etc.), *acids*, *bases*, and *salts*. To the chemist, therefore, any given substance is either an element, an oxide (sulphide, etc.), an acid, a base, a salt, or some combination of bodies belonging to these classes.

It has been stated previously (§ 2) that this treatise is a guide to the qualitative analysis of the commonly occurring substances, merely. The discussion will, therefore, be confined to the elements gold, platinum, silver, lead, mercury, copper, cadmium, bismuth, arsenic, antimony, tin, iron, chromium, aluminum, cobalt, nickel, manganese, zinc, barium, strontium, calcium, magnesium, lithium, sodium, potassium, the radical ammonium, their oxides and sulphides, and their salts with the following acids: HF , HCl , HClO_3 , HBr , HI , HNO_3 , H_2S , H_2SO_3 , H_2SO_4 , H_2CrO_4 , H_3BO_3 , H_3PO_4 , H_2SiO_3 , $\text{H}(\text{CN})$, $\text{H}_4\text{Fe}(\text{CN})_6$, $\text{H}_3\text{Fe}(\text{CN})_6$, H_2CO_3 , $\text{HC}_2\text{H}_3\text{O}_2$, $\text{H}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$.†

*Mechanical aggregates, or mixtures, need no discussion from the chemical point of view.

†It may be stated for the benefit of the student who has no acquaintance with Organic Chemistry that the last four formulas are those of *acetic*, *oxalic*, *tartaric*, and *citric* acids, respectively.

28. The analytic groups.—In determining a substance by analysis, we have to discover whether it is purely elemental or compound. If the latter, its *class* must be ascertained; and if it prove to be a salt, both the base and the acid involved in its formation must be identified. Considering only the twenty-six basic elements and the twenty-one acids mentioned above, it will be seen that the number of their possible combinations is quite large; and bearing in mind that a substance presented for analysis may be a mixture of several compounds, we would be overwhelmed by the difficulty of the problem were there no means of simplifying it. But fortunately two ways to this end have been found. The first lies in the fact that *all reactions are ionic* (§18) and, consequently, *all compounds formed in the course of analysis are combinations of ions*. Inasmuch as there are but few *kinds* of ions (§13), the identifying-properties to be learned are correspondingly limited. The second means lies in the fact that the basic ions may be readily separated by certain reagents into *five groups*, from which each member may in turn be isolated and then identified. The acidic ions are as readily identified as the basic ones; but no scientific grouping having yet been found for them, they are divided empirically into *four groups*.

THE BASIC-ION GROUPS

GROUP I.—This embraces the elements that form insoluble chlorides in an acidified solution: Ag, ¹Hg, [Pb]*. The group-reagent is HCl†; hence, this group may also be called *the hydrochloric-acid group*.

GROUP II.—This embraces the elements whose sulphides are insoluble in cold dilute-acid solution: ¹Hg, [Pb]; Cu, Cd, Bi; As, Sn, Sb; Au, Pt. The group-reagent is H₂S; hence, this group may also be called *the sulphuretted-hydrogen group*.

GROUP III.—This embraces the elements that form insoluble hydroxides or sulphides in ammonium hydroxide solution: Fe, Al, Cr;

*Lead chloride is somewhat soluble, and may appear in the next group also.

†The formula for an acid if printed in ordinary type will be read *dilute*; if in heavy type, *concentrated*.

Co, Ni; Mn, Zn. The group-reagent is $(\text{NH}_4)_2\text{S}$; hence, this group may also be called *the ammonium-sulphide group*.

GROUP IV.—This embraces the elements that form insoluble carbonates in the presence of NH_4Cl : Ba, Sr, Ca. The group-reagent is $(\text{NH}_4)_2\text{CO}_3$; hence, this group may also be called *the ammonium-carbonate group*.

GROUP V.—This embraces the elements whose chlorides, sulphides, and carbonates are soluble in the presence of NH_4Cl : Mg, Li, Na, K, $[\text{NH}_4]$. It may also be called *the alkali-metal group*.

THE ACID-ION GROUPS

GROUP A.—*The organic-acid group* embraces the following acids: $\text{HC}_2\text{H}_3\text{O}_2$, $\text{H}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$.

GROUP B.—*The barium-hydroxide group* embraces the following acids: H_2SO_4 , H_2SO_3 , H_2CrO_4 , H_3BO_3 , $\text{H}_2\text{C}_2\text{O}_4$.

GROUP C.—*The silver-nitrate group* embraces the following acids: HI, HBr, $\text{H}(\text{CN})$, $\text{H}_4\text{Fe}(\text{CN})_6$, $\text{H}_3\text{Fe}(\text{CN})_6$, HCl.

GROUP D.—*The original-substance group* embraces the following acids: HNO_3 , HClO_3 , H_3PO_4 , HF, H_2CO_3 , H_2S , H_2SiO_3 .

CHAPTER V

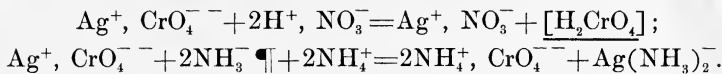
IDENTIFICATION OF THE BASIC IONS

29. Group I.—Members of this group may come to the analyst as the pure metal, as an alloy, as a salt, and (with the exception of silver) as an oxide. Sulphides and *minerals*—other than the oxides and the hydroxides—will be regarded in this book as salts.*

SILVER forms the colorless ions Ag^+ , $\text{Ag}(\text{NH}_3)_2^+$; Ag^- , $\text{Ag}(\text{CN})_2^-$.

Identification: † 1. With chlorine, silver is precipitated as AgCl , white and curdy, soluble in NH_4OH :— Ag^+ , $\text{Cl}^- + 3\text{NH}_3 \ddagger = (\text{NH}_3)_3\text{AgCl}$. § The solubility of the reaction product is due to its ready ionization, — $(\text{NH}_3)_3\text{AgCl} \rightarrow \text{Ag}(\text{NH}_3)_2^+$, NH_3^+ , Cl^- . From this solution, AgCl is again precipitated upon acidification by reason of the hydrogen ions of the acid combining with NH_3^+ , to form NH_4^+ , which unites with OH^- to produce $[\text{NH}_4\text{OH}]$, thereby increasing the concentration of Ag^+ and Cl^- (§ 26).

2. With CrO_4^{--} , silver is precipitated as Ag_2CrO_4 , brick-red and crystalline, soluble in HNO_3 and in NH_4OH :



MERCURY (^1Hg) forms the colorless ions Hg^+ and Hg_2NH_2^+ .

*For a description of the elements and their compounds, the student is referred to a standard work on General Chemistry.

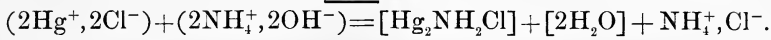
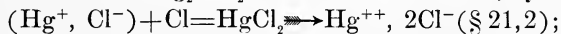
†Any insoluble, markedly colored, or strikingly odorific compound of an element may serve in general to identify it; but in practice we confine our attention to a few of the most notable ones.

‡Throughout this work, a line under a formula indicates the formation of a soluble product; a brace below indicates a precipitate; and a brace above means the evolution of a gas.

§It is doubtful if the compound NH_4OH actually exists. A solution of NH_3 in water is very slightly ionized into NH_4^+ , OH^- , due to the fact that NH_3 being less electro-positive than H^+ a complex ion NH_3H^+ is formed. A solution of the gas, therefore, holds the ions NH_3^+ , NH_4^+ , H^+ , OH^- and undissociated $[\text{NH}_4\text{OH}]$ and $[\text{H}_2\text{O}]$.

\P If the ammonia ion is less electro-positive than another positive ion present, it may behave as an anion (see last foot-note). This is a general rule for ions.

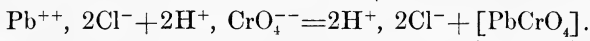
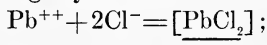
Identification: 1. With chlorine, ous-mercury is precipitated as HgCl , white and curdy, soluble in *aqua regia*, but transposed into mercurous chloramid, $\text{Hg}_2\text{NH}_2\text{Cl}$, black and insoluble, by NH_4OH :—



LEAD forms the colorless ions Pb^{++} , PbO_2^{--} , and $\text{PbOC}_2\text{H}_3\text{O}_2^-$.

Identification: 1. With chlorine, lead is precipitated as PbCl_2 , white and curdy, slightly soluble in cold water but very soluble in hot water.

2. From the above-mentioned aqueous solution, lead is reprecipitated by CrO_4^{--} as PbCrO_4 , bright yellow and flocculent-granular:—

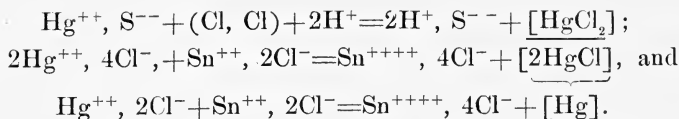


30. Group II.—Members of this group may come to the analyst in the elemental state, as an alloy, as a salt, and (excepting gold and platinum) as oxides.

LEAD may appear in this group in the course of analysis after the removal of members of the Hydrochloric-acid Group on account of the solubility of PbCl_2 . It must be removed before proceeding to analyse for members of the group proper. This is done by taking advantage of the fact that with SO_4^{--} PbSO_4 is precipitated, white, granular, and insoluble in the dilute-acid solution being used at the time. In this form, it is readily removed by filtration.

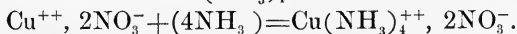
MERCURY (^{11}Hg) forms the colorless ions Hg^{++} and HgNH_2^{++} .

Identification: 1. With S^{--} (H_2S), ic-mercury is precipitated as HgS , black and granular, or whitish-yellow to brown if the reagent be not in excess, insoluble in **HNO₃** but soluble in *aqua regia*. If ous-mercury be present during the treatment with H_2S , it is transposed into HgS and Hg (§ 20, 2). The solution in *aqua regia* is reduced by SnCl_2 to HgCl or, if the reagent be in excess, to HgCl and Hg , this mixture appearing brown to black, owing to the formation of Hg_2O :—



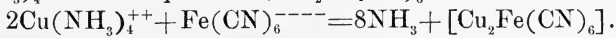
COPPER when univalent ($^{\text{I}}\text{Cu}$) forms the ions Cu^+ , and $\text{Cu}(\text{CN})_2^-$, colorless; and when bivalent ($^{\text{II}}\text{Cu}$), the ions Cu^{++} , blue, and $\text{Cu}(\text{NH}_3)_4^{++}$, intensely blue.

Identification: 1. Copper is precipitated by S^{--} in slightly-acid solution as CuS , black, flocculent-granular, slightly soluble in $(\text{NH}_4)_2\text{S}_x$, soluble in **HNO₃**. When this solution is diluted and treated with NH_4OH to excess, an intensely-blue color appears; this is due to the formation of $\text{Cu}(\text{NH}_3)_4^{++}$:—



2. The above-mentioned color is discharged by $\text{K}(\text{CN})$:—
 $\text{Cu}(\text{NH}_3)_4^{++} + 2\text{CN}^- + \text{K}^+ = 4\text{NH}_3 + \text{Cu}(\text{CN})_2\text{K} \rightleftharpoons \text{K}^+, \text{Cu}(\text{CN})_2^-.$

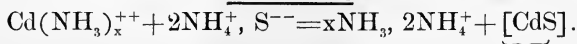
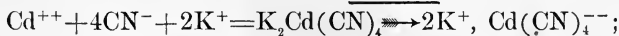
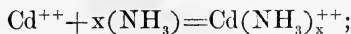
3. Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, precipitates from ammoniacal solution, even when too dilute to allow the blue color of the $\text{Cu}(\text{NH}_3)_4$ ions to be perceived, $\text{Cu}_2\text{Fe}(\text{CN})_6$, reddish brown:—



CADMIUM forms the colorless ions Cd^{++} , $\text{Cd}(\text{CN})_4^{--}$, and $\text{Cd}(\text{NH}_3)_x^{++}$.

Identification: 1. With S^{--} , cadmium is precipitated from slightly-acid solution as CdS , bright-yellow with a faint suggestion of green, flocculent, soluble in strong solutions of the halids and in hot **HNO₃**, insoluble in $\text{K}(\text{CN})$.

2. From a solution of one of its salts (as $\text{Cd}(\text{NO}_3)_2$), NH_4OH precipitates $\text{Cd}(\text{OH})_2$, white, flocculent, and soluble in excess of the reagent. Similarly, $\text{K}(\text{CN})$ precipitates $\text{Cd}(\text{CN})_2$, white, dissolving in excess of reagent. From these solutions, CdS is again precipitated by $(\text{NH}_4)_2\text{S}$ or H_2S :—



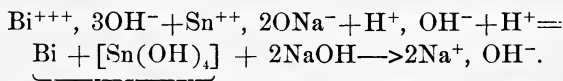
BISMUTH forms the colorless ions Bi^{+++} and BiO^+ , the latter rather strongly electropositive and the former but slightly so. Hence, salts of the trivalent ion readily hydrolyze (§ 25) to basic bismuthyl salts.

Identification: 1. With S^{--} in dilute acid solution, bismuth is precipitated as Bi_2S_3 , black, flocculent, insoluble in $(\text{NH}_4)_2\text{Sx}$, soluble in hot HNO_3 .

2. From a solution of one of its salts (as $\text{Bi}(\text{NO}_3)_3$), NH_4OH precipitates $\text{Bi}(\text{OH})_3$, white, flocculent, insoluble in excess of the reagent but soluble in dilute acid.

3. Upon forming BiCl_3 as just indicated in 2, and allowing it to drop slowly into cold water, BiOCl white and insoluble is formed by hydrolysis. The precipitation is facilitated by previous solution of NaCl in the water (§ 24, a).

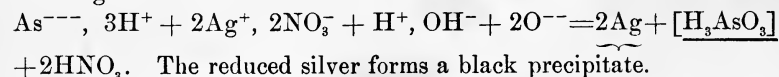
4. A stannite (as $\text{Sn}(\text{ONa})_2$) reduces the hydroxide to the elemental state, which will here show black:—



ARSENIC forms the colorless ions As^{---} , As^{-----} , AsO^{---} , AsO_4^{---} , and the colored (yellow) ions AsS_3^{---} , AsS_4^{---} .

Detection: 1. In slightly-acid solution, H_2S reduces ic-ions (if present) to ous-ions which are precipitated by S^{--} as As_2S_3 , lemon-yellow, flocculent, soluble in $(\text{NH}_4)_2\text{Sx}$ (by reason of the formation of AsS_3^{---}).* From this solution As_2S_3 is again thrown down upon acidification, soluble in $(\text{NH}_4)_2\text{CO}_3$ and in *aqua regia*. In the former case, the ions AsS_3^{---} are again formed, so that As_2S_3 reappears upon acidification; in the latter, As^{---} and As^{-----} ions are produced.

2. The *aqua regia* solution diluted and treated with zinc forms arsine, AsH_3 , in which the presence of arsenic may be shown by its reducing effect on a solution of silver nitrate:—

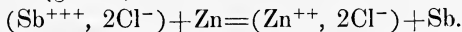


*The polysulphide $(\text{NH}_4)_3\text{AsS}_3$ ionizes thus— 3NH_4^+ , AsS_3^{---} ; and so for the other polysulphides.

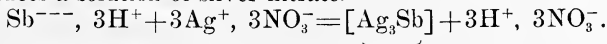
ANTIMONY forms the colorless ions Sb^{+++} , SbO^+ , SbO_2^- , SbO_3^- , SbO_3^{---} , SbO_4^{---} , $\text{SbOC}_4\text{H}_4\text{O}_6^-$ and the colored (reddish) ions SbS_3^{---} , SbS_4^{---} .

Detection: 1. In slightly-acid solution, H_2S reduces ic-ions, (if present) to ous-ions which are precipitated by S^{--} as Sb_2S_3 , orange-red, flocculent, soluble in $(\text{NH}_4)_2\text{Sx}$ (owing to the formation of SbS_3^{---})*. From this solution, Sb_2S_3 is again thrown down upon acidification, insoluble in $(\text{NH}_4)_2\text{CO}_3$, but soluble in *aqua regia*, owing to the formation of the ions Sb^{+++} and (possibly) Sb^{+++++} .

2. The *aqua regia* solution diluted and treated with zinc yields SbH_3 which is decomposed to some extent in the generator on account of the relatively weakly-electropositive character of antimony in comparison with zinc (§ 20, 1):—



This precipitate shows black; if relatively small in amount, it may all redissolve, react with the nascent hydrogen and pass out of the solution as SbH_3 with the portion that was not decomposed. The gas reduces a solution of silver nitrate:



Inasmuch as argentic stibnide is black, this test can only be made in the presence of arsenic by so diluting the *aqua regia* that the evolution of hydrogen is very slow. In this case, practically all the antimony is reduced in the generator. The contents of the generator are filtered, dissolved in **HCl**, diluted, and treated with H_2S . Antimony is precipitated as Sb_2S_3 . If arsenic has been removed before applying the stibine test and the silver nitrate solution shows a black precipitate, this is due to the formation of Ag_3Sb . It may be confirmed by filtering, dissolving the precipitate in **HCl**, diluting with an equal volume of water (which will precipitate AgCl), filtering, and treating the filtrate with H_2S .

TIN forms the colorless ions Sn^{++++} , Sn^{++} , Sn^{----} , $\text{Sn}(\text{OH})_3^-$, $\text{Sn}(\text{OH})_2^{++}$, SnOH^{+++} , SnO_2^{--} , SnO_3^{--} , and the colored ions SnS_2^{--} (brown), SnS_3^{--} (yellow).

* *vide* arsenic.

Identification: 1. In slightly-acid solution, S^{--} precipitates stannous-tin as SnS , dark-brown, flocculent; but stannic-tin is precipitated very slowly if cold and slowly if hot, as SnS_2 , white so long as the salt is in excess, then yellow and flocculent. These sulphides are soluble in $(NH_4)_2Sx$, owing to the formation of SnS_3^{--} .* From this solution, SnS and SnS_2 are again precipitated upon acidification, insoluble in $(NH_4)_2CO_3$, soluble in *aqua regia*, owing to the formation of Sn^{++++} .

2. The *aqua regia* solution diluted and treated with zinc precipitates tin, gray and spongy, on the zinc (§ 20,1). To confirm the test, filter, dissolve the residue (freed from obvious fragments of zinc) in HCl , and add the solution (2 or 3 cc.) to an equal volume of $HgCl_2$. A white ($HgCl$) or black to gray (Hg , $HgCl$) precipitate shows tin.

3. If antimony is present, it must be removed before applying test 2. This may be accomplished by effecting the reduction with a "voltaic couple" made by bending a strip of zinc so as to clasp a strip of platinum foil. This is dropped into the dilute *aqua regia* solution. The antimony then forms a black deposit adhering to the platinum, while the tin appears on the zinc but does not adhere to it.

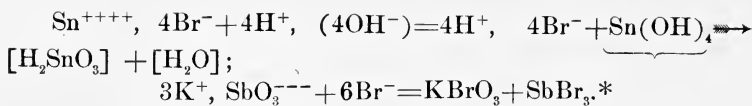
The foil is carefully removed, washed, and treated with a little $H_2C_4H_4O_6$, to which a few drops of HNO_3 have been added. The antimony dissolves, and is thrown down from this solution by H_2S . The tin is now tested for as directed in 2.

4. Tin and antimony may also be separated by taking advantage of the different behavior of their ions in bromine-water. The mixed sulphides precipitated from $(NH_4)_2Sx$ are dissolved in the least possible amount of *aqua regia*, diluted with an equal volume of water, and filtered ($=SbCl_4$ and $SnCl_4$). The filtrate is made strongly alkaline with boiling silica-free KOH :—



Bromine-water is now added to excess. Tin is precipitated as βH_2SnO_3 by hydrolysis, while antimony is transposed into soluble complexes:—

* $(NH_4)_2SnS_3$, etc., being formed by the reaction.



The stannic hydrate is white and flocculent. When this is removed by filtration, H_2S precipitates Sb_2S_3 from the filtrate.

GOLD forms the ions Au^+ , Au^{+++} , AuCl_4^- , AuO_2^- , AuS^- , AuS_2^- .

Identification: 1. With S^{--} , gold is precipitated in slightly-acid solution as Au_2S and Au_2S_2 , brown to black, soluble in $(\text{NH}_4)_2\text{Sx}$ owing to the formation of AuS_2^- and AuS^{--} , $((\text{NH}_4)_3\text{Au}_2\text{S}_3 \rightleftharpoons 3\text{NH}_4^+, \text{AuS}^-, \text{AuS}_2^{--})$. From this solution the sulphides are again thrown down upon acidification.

2. Soluble salts of gold (as H_2AuCl_4) are reduced by boiling with $(\text{NH}_4)_2\text{C}_4\text{O}_4$ and $\text{H}_2\text{C}_4\text{O}_4$ to the metallic state and precipitated, mixed with some β stannic acid (H_2SnO_3), as "the purple of Cassius" which shows violet, or brown, or brownish-violet.

PLATINUM forms the ions Pt^{++} , Pt^{+++} , PtCl_6^{--} , PtS_3^{--} .

Identification: 1. With S^{--} , platinum is precipitated in slightly-acid solution as PtS or PtS_2 , black, slowly soluble in $(\text{NH}_4)_2\text{Sx}$, and reprecipitated upon acidification.

2. Platinic salts are reduced by SnCl_2 to ous-salts, which dissolve in **HCl**, giving a deep-red color owing to the formation of the ion PtCl_6^{--} . If gold is present, it must be removed (Gold, 2) before applying this test.

31. Group III.—Members of this group may come to the analyst as the metal, as an alloy, as a salt, and as an oxide.

IRON forms the simple ions Fe^{++} , Fe^{+++} , FeO_4^{++} , and a number of complex ions, of which the most important are $\text{Fe}(\text{CN})_6^{--}$ and $\text{Fe}(\text{CN})_6^{---}$.

Detection: 1. Iron is precipitated from ous-salts by NH_4OH as $\text{Fe}(\text{OH})_3$, which is not soluble in $\text{Ba}(\text{OH})_2$, nor appreciably so in NaOH . This hydroxide is readily transposed by S^{--} , $((\text{NH}_4)_2\text{S})$, into ferrous sulphide, FeS , black, and readily soluble in cold dilute acid.

*The solution probably contains more complex compounds of antimony, also.

2. The ferrous chloride solution (1) is easily oxidized by boiling with a little **HNO₃** to FeCl₃ (§ 20, 3). From this solution, NH₄OH precipitates Fe(OH)₃, dark-brownish-red, gelatinous.

3. Solutions of ic-salts give with S(CN)⁻, (as KS(CN)), [Fe((CN)S)₃], deep-red and extremely soluble (§ 26). An excess of the reagent and the presence of an acid tend to intensify the color by antagonizing hydrolysis (§ 25).

ALUMINUM forms the simple ions Al⁺⁺⁺, AlO₂⁻, AlO₃⁻⁻⁻, and several complex ions containing the hydroxyl group.

Detection: 1. Aluminum is precipitated by OH⁻, (NH₄OH), as Al(OH)₃, white, gelatinous, and not appreciably soluble in an excess of this reagent (§ 24, a). It is not transposed by S⁻, (NH₄)₂S, into the sulphide, inasmuch as this compound is at once decomposed by hydrolysis:



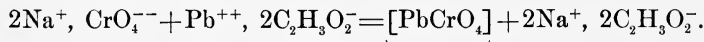
2. The hydrate, Al(OH)₃, dissolves in a solution of a stronger hydroxide (as Ba(OH)₂ and NaOH), owing to the fact that the relatively greater mass of more strongly-basic ions (Ba⁺⁺, Na⁺) rob it of OH⁻ (§ 24, b, 1). Since Al(OH)₃ ionizes to but a trivial degree, its chemical activity is slight (§ 18). From this basic-solution, Al(OH)₃ is again precipitated upon neutralization, or, what is more easily accomplished, after acidifying and then adding NH₄OH in excess (1).

CHROMIUM forms the ions Cr⁺⁺ (blue), Cr⁺⁺⁺ (violet), Cr(OH)₂O⁻ (green), CrO₄⁻ (yellow), Cr₂O₇⁻ (red). The ous-ions are readily oxidized to the ic-condition.

Identification: 1. Chromium in the ic-condition is precipitated by OH⁻, NH₄OH, as Cr(OH)₃, bluish-gray, gelatinous-flocculent, easily soluble in dilute acid, somewhat soluble in NH₄OH by reason of the formation of a soluble ammonia complex, and rather easily soluble in NaOH or KOH, owing to the formation of the ion Cr(OH)₂O⁻, (e. g., Cr(OH)₂ONa). Cr(OH)₃ is not transposed by S⁻, (NH₄)₂S, on account of hydrolysis.

2. Ic-compounds upon fusion with Na_2CO_3 yield Na_2CrO_4 , yellow and soluble.

3. A clear solution of a chromate (CrO_4^{--}) upon treatment with lead acetate gives a precipitate of lead chromate (PbCrO_4) bright-yellow and flocculent : —



COBALT forms the ions Co^{++} (rose-red), Co^{+++} (green), $\text{Co}(\text{NH}_3)_n^{++}$ (blue), $\text{Co}(\text{NH}_3)_3^{++}$, $\text{Co}(\text{NH}_3)_6^{+++}$, $\text{Co}(\text{NO}_2)_6^{---}$ (red).

Identification: 1. With OH^- , NH_4OH , ous-salts* give a bluish basic (NH_3) hydrate which changes on being heated to $\text{Co}(\text{OH})_2$, pink or rose-red, soluble in excess of the reagent and of NH_4Cl . Ammonium sulphide transposes the hydroxide, or a salt in alkaline solution, into CoS , black, insoluble in HCl (one part of acid to 10 parts water).

2. Oxides of cobalt color a bead of borax blue, owing to the formation of a borate. The CoS obtained in (1) may be used for this purpose, as an oxidizing flame ionizes the compound and burns the elements to SO_2 and CoO respectively.

NICKEL forms the ions Ni^{++} , $\text{Ni}(\text{NH}_3)_4^{++}$, $\text{Ni}(\text{NH}_3)_6^{++}$, $\text{NiC}_4\text{H}_4\text{O}_6^{--}$.

Identification: 1. With OH^- , NH_4OH , ous-salts give $\text{Ni}(\text{OH})_2$, pale-green, soluble in excess of the reagent, owing to the formation of basic (NH_3) ions. Ammonium sulphide, $(\text{NH}_4)_2\text{S}$, transposes these hydroxides into NiS , black, insoluble in HCl (1:10), but soluble in $(\text{NH}_4)_2\text{Sx}$, probably owing to the formation of complex basic (NH_3) ions. This solution is brown to violet in color. Hence, *the $(\text{NH}_4)_2\text{S}$ used must be freshly prepared* so as to avoid the presence in it of any $(\text{NH}_4)_2\text{Sx}$; and the previous treatment with NH_4OH should be carried *barely beyond neutrality* so as to avoid as far as possible the formation of nickel-ammonia ions and ammonium salts.

2. Oxides of nickel color a borax-bead violet to reddish-brown. The sulphide (1) may be used for this purpose. The presence of cobalt may mask this test.

*The common compounds of cobalt are of the ous-form.

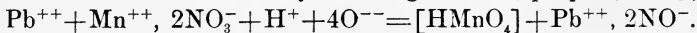
3. Nickel (sulphide) (1) may be separated from cobalt (sulphide) by taking advantage of the differing solubilities of their ic-hydroxides in NH_4OH . To accomplish this, the mixed sulphides are dissolved in the least possible amount of hot HCl , to which a little HNO_3 has been added, boiled till the liquid is nearly all evaporated, and NaOH then added to strongly-alkaline reaction. The hydroxides at first precipitated by the last reagent dissolve in an excess of it. The solution is now diluted with an equal volume of bromine water and again boiled. This oxidizes the ous-hydroxides to the ic-form, and they are precipitated as a black powder. This is allowed to settle, the fluid decanted, and the precipitate washed by decantation. On boiling the precipitate with NH_4OH , $\text{Ni}(\text{OH})_3$ goes into solution. It is filtered from the $\text{Co}(\text{OH})_3$, and nickel is then precipitated from the filtrate by H_2S . This precipitate may then be tested further as directed in 2.

MANGANESE forms the ions Mn^{++} (pink), Mn^{+++} , MnO_4^{--} (green anion of manganates), MnO_4^- (purple anion of permanganates).

Detection: 1. With OH^- , NH_4OH , ous-salts give $\text{Mn}(\text{OH})_2$, white, but readily oxidizing upon standing in solution to $\text{Mn}(\text{OH})_3$, which is brownish. The precipitation is incomplete, owing to the fact that $\text{Mn}(\text{OH})_2$ is more strongly basic than NH_4OH (§ 18); and if ammonia salts are present, no precipitation occurs (§ 24, b, 1)*. Ic-salts with OH^- yield $\text{Mn}(\text{OH})_3$ more weakly basic than $\text{Mn}(\text{OH})_2$. $(\text{NH}_4)_2\text{S}$ transposes these hydroxides (and salts in alkaline solution) into MnS , flesh-pink, flocculent-gelatinous, easily oxidized (by exposure to the air) to readily soluble MnSO_4 , and soluble in dilute acid.

2. Salts of manganese (MnS from 1 will answer) fused on a platinum foil with Na_2CO_3 and KNO_3 give a blue-green "melt," due to the formation of a manganate (MnO_4^{--}).

3. Manganese compounds dissolved in HNO_3 and oxidized by one of the common oxides of lead yield manganic acid, purple (MnO_4^-):—



For the same reason Fe^{++} is incompletely, and Mg^{++} not at all, precipitated by NH_4OH in presence of NH_4Cl .

Reducing agents (as zinc) should be removed before applying this test.

ZINC forms the colorless ions Zn^{++} , ZnO_2^{--} , and complex ammonia-ions, $\text{Zn}(\text{NH}_3)_n^{++}$.

Identification: 1. With OH^- , NH_4OH , zinc salts yield $\text{Zn}(\text{OH})_2$, white, gelatinous, soluble in excess of the reagent owing to the formation of zinc-ammonia ions. This hydroxide (and the complex salts in ammoniacal solution) are transposed by $(\text{NH}_4)_2\text{S}$ (or the ion S^{--}) into ZnS , white to grayish-white, and easily soluble in dilute HCl .

2. Solutions of zinc salts (as ZnCl_2 from 1) treated with Na_2CO_3 yield basic zinc carbonate ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2\text{H}_2\text{O}$) by hydrolysis of the carbonate which is first thrown down. The precipitate is white and insoluble in excess of the reagent.

32. Group IV.—Members of this group may come to the analyst as a salt and as an oxide.

BARIUM forms the colorless ion Ba^{++} .

Identification: 1. With CO_3^{--} , $(\text{NH}_4)_2\text{CO}_3$, barium is precipitated from alkaline solution as BaCO_3 , white and flocculent but becoming pulverulent-crystalline on standing, easily soluble in acids. The presence of NH_4Cl affects this precipitate but trivially, since Ba^{++} is more strongly basic than NH_4^+ (§ 18).

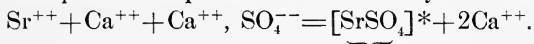
2. The acetate yields with CrO_4^{--} , (K_2CrO_4), BaCrO_4 , light-yellow, soluble in **HCl**; and from this solution SO_4^{--} , (H_2SO_4), precipitates BaSO_4 , white.

STRONTIUM forms the colorless ion Sr^{++} .

Identification: 1. With CO_3^{--} , strontium is precipitated from alkaline solution as SrCO_3 , white and flocculent but becoming pulverulent-crystalline on standing, not affected appreciably by NH_4Cl , and easily soluble in acids.

2. The chloride yields SrSO_4 with SO_4^{--} , white, pulverulent-crystalline. In applying this test barium and calcium must be absent. The former may be removed by taking advantage of the relative insolubility of its chromate in acetic acid (2, above), and the latter by

effecting the sulphate transposition of the Sr^{++} by means of CaSO_4 :—



CALCIUM forms the colorless ion Ca^{++} .

Identification: 1. An ammoniacal solution free of Ba^{++} and Sr^{++} (see Strontium 2, above) yields with $\text{C}_2\text{O}_4^{--}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, calcium oxalate (CaC_2O_4), white and finely pulverulent-crystalline.

33. Group V.—Members of this group may come to the analyst as the metal (magnesium only), as an alloy (Mg, Na, K, NH_4 —the last three as *amalgams*), as a salt, as an oxide (Mg only), and as hydroxides.

MAGNESIUM forms the colorless ion Mg^{++} .

Identification: 1. Magnesium is arbitrarily separated from its chemical congeners of Group IV by the fact that the carbonate is not precipitated in the presence of NH_4Cl .† Thus it is brought by the scheme of analysis (Chap. IV) into Group V. From this solution, it is precipitated (by adding NH_4OH , to strong alkalinity, and then Na_2HPO_4) as MgNaPO_4 and MgNH_4PO_4 , white and finely crystalline.

Before applying this test, members of Group IV must be *completely removed*, as they yield under the above treatment a *flocculent* precipitate that may obscure that of magnesium.

LITHIUM forms the colorless ion Li^+ .

Identification: The lithium ion colors a Bunsen flame‡ bright-red, masked by sodium. If sodium is present, the flame observed through the spectroscope shows a scarlet line at the left of the sodium line.

SODIUM forms the colorless ion Na^+ .

Identification: The sodium ion colors the flame intensely yellow. When this is observed through the spectroscope, a bright-yellow band is seen at solar D. On account of the universal occurrence of sodium,

* Solubility of SrSO_4 and CaSO_4 in H_2O — $1\text{SrSO}_4:1000\text{H}_2\text{O}$; $1\text{CaSO}_4:400\text{H}_2\text{O}$.

† See § 24 and § 31, *manganese*, 1, foot-note.

‡ Salts of the alkalis are as a rule soluble. Hence, for their identification we rely upon the well-known fact that they impart characteristic colors to the flame.

it is only reported as a component of an assay when the yellow color of the flame or spectrum is intense and continued for some time.

POTASSIUM forms the colorless ion K^+ .

Identification: The potassium ion colors the flame violet-red, masked by sodium. To eliminate the latter, the flame is observed through a cobalt (blue) glass.

AMMONIUM forms the colorless ion NH_4^+ .

Identification: 1. Ammonia (NH_3) is expelled from its compounds by the fixed alkalis (§ 24) and recognized by its odor, when in quantity, or by changing the color of red litmus-paper to blue.

NOTE.—Having read the book consecutively to this point, the student will now pass to Chapter VIII.

CHAPTER VI

SYSTEMATIC ANALYSIS FOR THE ACIDIC IONS THEIR IDENTIFICATION

34. The acids likely to be met with in the course of an ordinary analysis are the following: Acetic, oxalic, tartaric, citric; sulphuric, sulphurous, chromic, boric; hydroiodic, hydrobromic, hydrocyanic, hydroferro-cyanic, hydroferri-cyanic, hydrochloric; nitric, chloric, phosphoric, hydrofluoric, carbonic, hydrosulphuric, silicic. These acids are divided into the four groups named in § 28 by the tests indicated below. In the systematic analysis of a substance, unless it is distinctively a metal in appearance it is assumed to be a salt. If no acid is found (and the substance is not a metal), it is an oxide or an hydroxide; but it is still technically termed "a salt." The portion of the salt taken for analysis is called *the assay*.

35. Grouping and identifying the acid.—In order to locate the group of the acid, we proceed in the following manner:—

1st. Heat a small portion of the assay—about 0.5 of a gram—on a platinum foil or a porcelain-crucible lid, very gently at first and then more strongly, and look for signs of charring. The student must be careful not to mistake mere change of color (blackening) for charring. A little preliminary practice with sugar will enable him to recognize the change meant. If charring occurs, notice the odor; if it is like that of burnt sugar, organic acids may be present. Proceed as directed in A.*

If the above tests are not given, organic acids are absent. Proceed to test for the next group.

2nd. Powder finely 1 g. of the assay, transfer it to a porcelain dish, add 5 g. Na_2CO_3 crystals and 15 cc. distilled water, boil 10 minutes, replacing the water occasionally as it evaporates, dilute to 30 cc., and

*But let the student remember that oxalates do not char, while some organic compounds other than the acids and their salts do. Oxalic acid will be found, however, in B, if present.

then filter in case the solution is not clear or a residue remains. This treatment assures the transposition of acids of Group B into soluble sodium salts. Acidify a small portion with H_2SO_4 . If a yellow or orange precipitate appears (sulphides of As, Sb, Sn), acidify about half of the solution, filter, boil till H_2S is all expelled, and label it X. Label the other half of the solution Y.

Put about 3 cc. of Y into a small conical flask, add HCl dropwise with constant shaking till effervescence ceases and the solution is *slightly* acid, boil vigorously to expel absorbed CO_2 , and cool by allowing a stream of water to flow over the flask. Then add $\text{Ba}(\text{OH})_2$ to slight alkalinity and *at once* tightly stopper the flask. If at the end of 5 minutes a precipitate appears, acids of the barium-hydroxide group are present. Proceed as directed in B.

If no precipitate forms, the barium-hydroxide acids are absent. Proceed to test for the next group.

3rd. Utilize X and Y from the preceding group, if any remains; otherwise, make some afresh. Acidify 2-3 cc. of X (or of Y if there be no X) with HNO_3 and add a few drops of AgNO_3 . If a precipitate appears, acids of the silver-nitrate group are present. Proceed as directed in C*

If no precipitate forms, the silver nitrate acids are absent. Proceed to test for the next group.

4th. Portions of the "original substance" are used in testing for members of the fourth group. Proceed as directed in D.

A.—ORGANIC GROUP

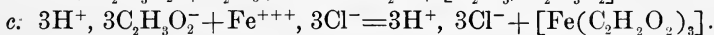
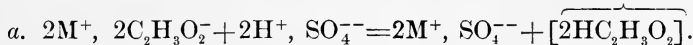
1. $\text{HC}_2\text{H}_3\text{O}_2$.—*a.* Treat 1 g. of the dry salt in a test tube with about 5 cc. of H_2SO_4 , and warm gently. The presence of acetic acid is revealed by its well-known pungent odor.

b. At once add 2-3 cc. of $\text{C}_2\text{H}_5\text{OH}$ and a few drops of H_2SO_4 to the contents of the tube and heat to boiling. Acetic acid is revealed by the ethereal, fruity odor of ethyl acetate.

c. Boil 1 g. of the salt a minute or so with 5 cc. of H_2O , filter, and add a drop of FeCl_3 to the filtrate. Acetic acid is revealed by the

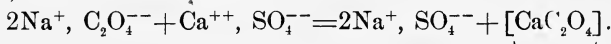
*A white precipitate indicates either of the first five; a colored precipitate indicates $\text{H}_3\text{Fe}(\text{CN})_6$ or H_2CrO_4 ; but if H_2S is present, all these precipitates may be black.

formation of a deep-red coloration. On boiling, $\text{Fe}(\text{OH})_3$ is precipitated by hydrolysis.



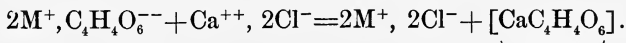
2. **$\text{H}_2\text{C}_2\text{O}_4$** .—Put 2 g. of the dry salt in a porcelain dish with 15 cc. of distilled H_2O , add 5 g. of Na_2CO_3 crystals, and boil for 10 minutes, replacing the water as it evaporates. Filter, and label the filtrate Z.

Acidify 2 cc. of Z with $\text{HC}_2\text{H}_3\text{O}_2$ and add a few drops of CaSO_4 . The presence of oxalic acid is revealed by a white, finely-pulverulent precipitate. If no precipitate appears after heating and standing 10 minutes, oxalic acid is absent.



3. **$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$** .—Acidify the remainder of Z with HCl , and boil to expel absorbed CO_2 . Add NH_4OH to bare alkalinity, boil,* then add 1-2 cc. of NH_4Cl , and then about 2 cc. of CaCl_2 . Shake vigorously, and allow to stand 10 minutes. Tartaric acid is revealed by a white precipitate. *Confirm the test*, thus: Filter, and reserve the filtrate for 4. Wash the precipitate with hot water, transfer it to a porcelain dish, add 5 cc. NaOH , and stir well for a minute. The precipitate dissolves. Dilute to 15-20 cc., and boil. The separation of a white precipitate proves the presence of tartaric acid.

If no precipitate is given by CaCl_2 , tartaric acid is absent.



The presence of NH_4Cl facilitates the precipitation of $\text{CaC}_4\text{H}_4\text{O}_6$ by the NH_4 ions robbing $\text{Ca}(\text{OH})_2$ —formed by hydrolysis—of OH ions to make relatively undissociated $[\text{NH}_4\text{OH}]$, thus keeping the mass of Ca ions relatively great. Calcium tartrate dissolves in a concentrated solution of NaOH , owing to the formation of undissociated solu-

*After expelling excess of NH_3 the solution is neutral, and oxalic acid, if present, will not be precipitated appreciably by CaCl_2 .

ble complexes; but it is reprecipitated upon dilution on account of reionization in which Na^+ and OH^- remain practically in the ionic state while Ca^{++} and $\text{C}_4\text{H}_4\text{O}_6^{--}$ reunite.

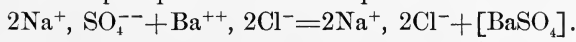
4. $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$.—Concentrate the filtrate from 3 by evaporation to about 5 cc., filter if not clear, mix with three times its volume of $\text{C}_2\text{H}_5\text{OH}$, and add a few drops of CaCl_2 . The formation of a white precipitate points to citric acid. *Confirm the test*, thus: Filter, wash with alcohol, and dissolve on the filter with the least possible amount of HCl , add NaOH to alkalinity, and boil. The separation of a heavy white precipitate shows the presence of citric acid.

If no precipitate is obtained, citric acid is absent.

Calcium citrate is quite soluble in water but not in alcohol.

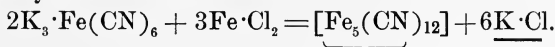
B.—BARIUM-HYDROXIDE GROUP

5. H_2SO_4 .—Acidify 2 cc. of Y with HCl , and add a drop of BaCl_2 . A white precipitate indicates sulphuric acid.

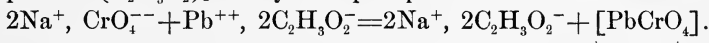


6. H_2SO_3 .—Acidify 2 cc. of Y with HCl and *immediately* expose to the evolved gas a drop of a mixture of ferric chloride solution and potassium ferricyanide solution—equal parts—in the loop of a platinum wire. A blue precipitate in the drop of reagent indicates sulphurous acid. If H_2S is present (D), some $\text{HC}_2\text{H}_3\text{O}_2$ should be introduced into Y before its complete acidification with HCl .

Sulphurous acid reduces Fe^{+++} to Fe^{++} ; and with ferrous salts a ferricyanide yields *Turnbull's blue*:



7. H_2CrO_4 .—Acidify 2 cc. of Y with $\text{HC}_2\text{H}_3\text{O}_2$ and add a few drops of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. A yellow precipitate shows chromic acid.



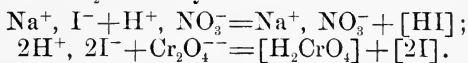
8. H_3BO_3 .—Evaporate 2-3 cc. of Y to dryness, cool, moisten with 2 or 3 drops of H_2SO_4 , add a little glycerine, mix with the glass rod, and bring some of the mixture into a colorless flame on a clean platinum wire. A green color imparted to the flame shows boric acid.

Sulphuric acid liberates H_3BO_3 from the solution ($\text{Na}_2\text{B}_4\text{O}_7$), and this reacts with glycerine to form an etherial salt that is easily decomposed by heat. The boron ion colors the flame.

9. $\text{H}_2\text{C}_2\text{O}_4$.—If no other acid of this group has been found, the group test will be ascribed to oxalic acid. Proceed as directed above (A, 2).

C.—SILVER-NITRATE GROUP

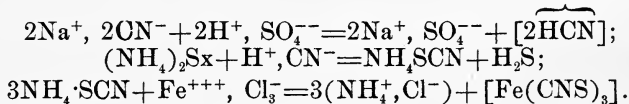
10. HI.—To 2 cc. of X (or of Y if there is no X) add 2 cc. of HNO_3 , 2 or 3 drops of K_2CrO_4 , and 2 cc. of CS_2 , and shake. A violet color in the CS_2 shows hydroiodic acid.



11. HBr.—*a. HI is absent:* Utilizing the solution used in 10, pass a few bubbles of chlorine gas through it, and shake. A yellowish-red color in the CS_2 (Br) shows hydrobromic acid.

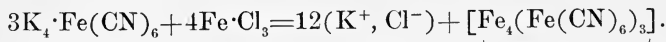
b. HI is present: If HI was found in 10, it must be removed before testing for HBr. This is done by filtering out the iodine-saturated CS_2 by passing the fluid through a wet filter. The CS_2 remains on the filter. Treat the filtrate again with HNO_3 , K_2CrO_4 , and CS_2 , filter, and repeat till no further trace of iodine is seen. Now treat the clear filtrate with chlorine gas and CS_2 , as directed in *a*.

12. $\text{H}(\text{CN})$.—Acidify 2-3 cc. of Y with H_2SO_4 ,* and immediately expose to the evolved gas a drop of $(\text{NH}_4)_2\text{S}$ in the loop of a platinum wire supported in a cork which rests loosely on the mouth of the test tube. After 10 minutes shake the drop onto a porcelain crucible lid, evaporate it to dryness at *very gentle heat*, and touch the residue with a drop of FeCl_3 . A deep-red coloration shows hydrocyanic acid.



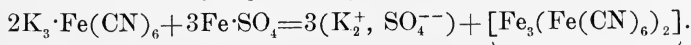
*Hydrocyanic acid gas is extremely poisonous. Hence, the tube for its generation should be arranged under the hood before adding the H_2SO_4 . Cyanides will not be given the student as an "unknown" for determination. If a practicing chemist has reason to suspect the presence of this acid in a substance, he assures himself upon the point by making the above test before taking any odor evolved in the course of the analysis.

13. $\text{H}_4\text{Fe}(\text{CN})_6$.—Acidify 2 cc. of X (use Y if there be no X) with H_2SO_4 and add a drop of FeCl_3 . A blue precipitate (Prussian blue) shows hydroferrocyanic acid.



If HI is present it must be removed (11, *b*) before applying this test, as otherwise it may reduce Fe^{+++} to Fe^{++} and thus prevent the reaction.

14. $\text{H}_3\text{Fe}(\text{CN})_6$.—Prepare a little fresh FeSO_4 by treating a small quantity of iron filings with H_2SO_4 . Add a drop of this to 2 cc. of X (use Y if there be no X) acidified with H_2SO_4 . A dark-blue precipitate (Turnbull's blue) shows hydroferricyanic acid. A *light-blue color* will be caused by $\text{H}_4\text{Fe}(\text{CN})_6$, if present (13).



15. HCl .—If neither HI, HBr, $\text{H}(\text{CN})$, or $\text{H}_4\text{Fe}(\text{CN})_6$ has been found *and the group-test was a white precipitate*, it can be due to hydrochloric acid only, and no further test for it need be made.

If the group-test gave a black precipitate (H_2S), cover it with NH_4OH in a porcelain dish, mix well with the glass rod, filter, and acidify the filtrate with HNO_3 . A white precipitate shows hydrochloric acid.

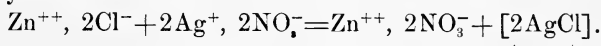
If any acid of the group specified above has been found in the course of analysis, it must be removed before testing for HCl. Proceed thus: Acidify 5–10 cc. of X (use Y if there be no X) with HNO_3 , add 2 cc. of AgNO_3 , shake well, decant the liquid through a filter, wash the precipitate twice by shaking it with water, pouring the decantations through the same filter, and test the precipitate in the following manner:—

a. HI only was found: Stir the precipitate thoroughly with NH_4OH , filter, and acidify the filtrate with HNO_3 . A white precipitate shows hydrochloric acid.

b. HBr was found, and HCN is absent: Cover the precipitate in a test tube with $(\text{NH}_4)_2\text{CO}_3$, pass CO_2 through the mixture for a short

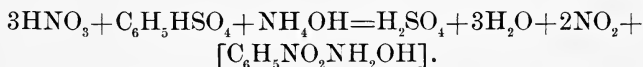
time, warm (do not boil) the mixture with occasional shaking for 10 minutes, filter, and acidify the filtrate with HNO_3 . A white precipitate shows hydrochloric acid.

c. HCN, or $\text{H}_4\text{Fe}(\text{CN})_6$, or $\text{H}_3\text{Fe}(\text{CN})_6$ was found: Dry the precipitate in a porcelain crucible by gentle heat (below 100°), then ignite to low redness, and cool. This breaks up the cyanogen compounds and expels their $(\text{CN})^-$. Cover the residue with a piece of zinc in close contact, add 5 cc. H_2SO_4 , and allow the metathesis to continue an hour. This reduces AgCl to $[\text{Ag}]$ and ZnCl_2 . Pour off the liquid and add to it a few drops of AgNO_3 . A white precipitate shows hydrochloric acid.



D.—ORIGINAL-SUBSTANCE GROUP

16. HNO_3 .—*a. H_2CrO_7 was not found (in Y):* To a little of the salt on a crucible lid, add a drop of phenol-sulphonic acid and then a drop or so of NH_4OH . An intense yellow color reveals the presence of nitric acid.



b. H_2CrO_4 was found (7): Nearly (but not quite) neutralize 2 cc. of Y with HCl , add $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and filter off the PbCrO_4 . Evaporate a few drops to dryness on a crucible lid at gentle heat (not above 100°), and test the residue as directed in *a*.

17. H_2CO_3 .—Treat 1 g. of the salt in a test-tube with HCl . If it dissolves with effervescence, hold a drop of $\text{Ba}(\text{OH})_2$ in the loop of a platinum wire in the escaping gas. The formation of a white precipitate (BaCO_3) shows carbonic acid.

18. HF .—Mix about 0.5 g. of the powdered salt with an equal bulk of pulverized fused KHSO_4 , transfer the mixture to a small ignition tube and heat it strongly for a minute. With a file cut off the ignition-tube below the top of the assay, wash out the tube and dry it in the flame. The presence of an opaque ring of etched glass a little above where the assay stood shows hydrofluoric acid.

19. H_2S .—*a. Cyanogen acids are absent:* Treat 1 g. of the salt in a test-tube with HCl. Hydrosulphuric acid is revealed by its well-known odor.

b. Cyanogen acids are present (12, 13, 14): Hold a strip of filter paper freshly dipped into $Pb(C_2H_3O_2)_2$ in the gas obtained as directed in *a*. The blackening of the paper (PbS) shows H_2S .

If the substance for analysis contains a *soluble sulphide*, the presence of H_2S will have been indicated in making the general test for Group II. If the salt contains certain sulphides insoluble in water but capable of metathesis with a solution of Na_2CO_3 , the general test for Group III will be black (see foot-note). If H_2S was found at either of these stages of the work, it is not necessary to make the tests detailed above (*a*, *b*).

20. $HClO_3$.—Boil 1 g. of the salt with 5 cc. of water, filter, render the filtrate faintly blue with indigo, and acidify with H_2SO_4 . Chloric acid, if present, reveals itself by bleaching the solution.

21. H_3PO_4 .—Dissolve 0.5 of the salt in HNO_3 at gentle heat, add an equal volume of water, filter if not clear or a residue remains, and evaporate the filtrate almost to dryness. If a solid separates in process of evaporation, redissolve it in the least possible amount of water.

a. As, Sb, and Sn are present (§ 37, II, 1, 2) but $H_4Fe(CN)_6$ is absent (13): Remove these metals by heating the solution and passing H_2S till it occasions no further precipitation. Filter through a small wet paper. Boil the filtrate till H_2S is all expelled, and add 0.5 cc. of the solution to 4 cc. of $(NH_4)_2 MoO_4$. A yellow precipitate shows phosphoric acid.

b. $H_4Fe(CN)_6$ is present: If As, Sn, Sb are present, remove them as shown in *a*, and then remove ferrocyanic acid from the filtrate; if they are absent, remove ferrocyanic acid from the solution at once, thus: Treat the solution with $ZnSO_4$ till no further precipitation occurs, filter, and test the filtrate as in *a*.

c. The metals and acids named above are all absent: At once treat the solution obtained as directed in the first paragraph with $(NH_4)_2 MoO_4$, as shown in *a*.

22. H_2SiO_3 .—Boil 2 g. of the salt with 20 cc. of water for 5 minutes. Filter, and reject the filtrate. Dry the residue, pulverize it, and fuse 0.2–0.5 of a gram of it in a platinum cup (or on platinum foil) with three times its bulk of mixed Na_2CO_3 and KNO_3 (3:1). Keep it in a state of fusion for at least 5 minutes. Dissolve the melt by boiling in 5 cc. of water, filter if not clear, and acidify with HCl . A flocculent white precipitate indicates silicic acid. *Confirm the test* by evaporating the fluid with its precipitate to dryness, igniting, covering with water and rubbing any insoluble portion in the bottom of the dish with a glass rod. If H_2SiO_3 (now SiO_2^{f}) is present, a distinct grittiness will be perceived.

CHAPTER VII

SYSTEMATIC ANALYSIS FOR THE BASIC IONS

36. In beginning the analysis for basic ions, two cases may arise—*i*. The substance is distinctly metallic; *ii*. The substance is obviously not metallic.

i. SOLUTION OF A METAL.*—Treat 0.25–1.0 g. of the metal with HNO_3 and (unless solution in the cold acid begins freely at once) heat to boiling:—

a. *Solution is complete*: This shows Au, Pt, Sn, and Sb are certainly absent. Dilute with eight volumes of water and proceed as directed in I.

b. *A metallic residue will not dissolve*: Decant the nitric-acid solution, wash the residue with a little water, and add the wash-water to the decanted acid-solution. Evaporate a few drops of this solution in a porcelain dish. If a solid residue is left, proceed with the solution as directed in *a*.

The metallic residue is next dissolved in a little *aqua regia*, diluted with 8 volumes of water, and tested for gold and platinum (II, 7).

c. *The metal dissolves, and a white powder is formed in the process*: Dilute with water and boil; if the solution clears up, proceed as directed in *a*. If a precipitate still remains, Sn or Sb is present (H_2SnO_3 , HSbO_3). Filter, wash the precipitate on the filter twice with hot water, adding the first wash-water to the filtrate. Label this solution "I." Now puncture the bottom of the filter with the glass rod and wash the precipitate into a small conical flask with spurts of water from the wash-bottle, heat to boiling, and saturate with H_2S . A colored precipitate (orange, red, yellow, brown) indicates antimony or tin or both. To separate and identify each when both occur, treat this precipitate as directed in II, Arsenic Sub-group, 2.

Now proceed with the filtrate labeled "I" as directed above in *b*.

*This includes alloys.

d. *The metal dissolves, leaving a black powder:* This is carbon (graphite). Collected and heated on a platinum foil, it burns without residue. Iron and some other alloys may contain a considerable amount of graphite.

ii. SOLUTION OF A SALT.*—a. *The substance dissolves in water:* Treat 0.5 g. of the substance in a test-tube or small conical flask with 15 cc. of water, stopper with the thumb and shake thoroughly. If complete solution ensues, proceed as directed in I; if solution is not complete in cold water, boil till the fluid becomes clear and then proceed as directed in I.

b. *The assay does not dissolve in water but does so in hydrochloric acid:* Having tried the effect of water as directed in a, and a residue remaining, allow the solid to subside, decant the water through a filter and evaporate a few drops in a porcelain dish or on a platinum foil. In case a solid residue is left from evaporation, label the water-solution "I" for subsequent treatment as directed in a; if there is no residue from evaporation, reject the water. To the residue not affected by water, add 5 cc. HCl and boil; if it dissolves completely, dilute to 30 cc. with water and proceed as directed in II. In case HCl does not effect complete solution, allow subsidence to occur, decant the fluid through a filter, evaporate a few drops in order to determine if any solution has been effected; if so, label it "Dil. HCl;" if not, reject the filtrate. Now treat the residue not affected by HCl with 5 cc. of **HCl**, and boil. If it dissolves completely, dilute to 20 cc., add the partial solution (if any) obtained with HCl, and proceed as directed in II.

c. *The assay non-soluble in water and hydrochloric acid dissolves in nitric acid:* A residue remaining after treatment with water and hydrochloric acid as directed above may dissolve in nitric acid. Decant the hydrochloric acid and wash the assay by shaking it with 15 cc. of water, allowing subsidence to occur and then decanting the water. Now cover the assay with 5 cc. **HNO₃**, and boil. Unless solution is complete, pour off a few drops of the acid, dilute with an equal volume of water, and evaporate; if a solid residue is left, decant

*This word is here used technically (see § 34).

all the nitric acid, dilute to 30 cc., and label 'I' for subsequent treatment as in *a*. If solution was complete, dilute to 30 cc., and proceed as directed in I.

d. The assay non-soluble in H_2O , HCl , HNO_3 dissolves in aqua regia: Treat a residue remaining after trying the methods *a*, *b*, *c*, with *aqua regia*. If solution occurs, dilute to 30 cc., and proceed as directed in II.

e. The assay is not affected by water or acids: Pulverize 0.5 g. of the salt and fuse it with 3 times its bulk of the mixture Na_2CO_3 (three parts) KNO_3 (one part) in a platinum spoon. Dissolve the melt by boiling in 15 cc. of water, and filter if not clear. Acidify with HNO_3 . If no precipitate occurs, proceed as directed in I. If a precipitate occurs (H_2SiO_3 , S, H_2SnO_3 , $HSbO_3$), filter, and label the filtrate 'I' for subsequent treatment as directed in *a*. If the precipitate is light-yellow and burns with a pale-blue flame with evolution of SO_2 , it points to the salt's being a poly-sulphide; if silicic acid has previously been found (§ 35, 22), it will appear here also. But if the precipitate is voluminous and white, tin and antimony are probably present. Test it as shown in *i*, *c*.

37. Grouping and identifying the basic ions.—

I.—HYDROCHLORIC-ACID GROUP

To the solution 'I' (obtained by methods detailed in section 36), add 1-2 cc. HCl , stopper and shake thoroughly. If no precipitate appears, members of this group (Ag, Pb, Hg) are absent; proceed to Group II. If a precipitate is formed, filter, and test the filtrate with a drop of HCl . If it remains clear, precipitation is complete; otherwise you must repeat the process of precipitation and filtration until no cloudiness is observed upon addition of a drop of the reagent. Label the filtrate 'II'.

1. LEAD: Wash the precipitate on the filter with 5 cc. of boiling water, and add K_2CrO_4 to the filtrate. A yellow precipitate shows lead (§ 29). *However, lead may be present and not show itself here.*

2. OUS-MERCURY: Pour about 3 cc. of NH_4OH over any residue

left on the filter. If it turns black, monovalent mercury is shown (§ 29).

3. SILVER: Acidify the ammonia filtrate with HCl. A white precipitate shows silver (§ 29).

II.—SULPHURETTED-HYDROGEN GROUP

The filtrate from I (or solution "II", § 36) must be moderately concentrated (§ 26, second paragraph), only slightly acid, and free from an oxidizing acid (HNO_3); because, *first*, H_2S being a weak acid its dissociation is repressed by a stronger acid (§ 24), and, *second*, an oxidizing acid decomposes it:



In case HNO_3 is present, evaporate to complete dryness, ignite the residue (nitrates are decomposed at red heat), cool, dissolve the residue in a little HCl, dilute to 30-40 cc.,* pour 5 cc. into a test-tube labeled "Au-Pt," and reserve. Saturate the remainder with H_2S .† If no precipitate appears, members of this group (Pb, $^{\text{II}}\text{Hg}$, Cu, Cd, Bi, As, Sn, Sb, Au, Pt) are absent; proceed to Group III. If a precipitate is formed, filter, and test the filtrate with H_2S till precipitation is complete. Wash the precipitate with hot water, add the first washing to the filtrate and label it "III."

If HNO_3 is not present, reserve 5 cc. for gold and platinum, and saturate the rest with H_2S , etc., as above.

SEPARATION OF THE ARSENIC SUB-GROUP.

Loosen the edges of the filter, lift it from the funnel to the palm of one hand and unfold it so that it lies flat, cover it with a small porcelain dish, and by a quick reversal of the hands bring the filter uppermost. Beginning at the edge of the filter, press the paper gently, so as to cause the precipitate to adhere to the dish, and then taking the paper by one edge strip it from the precipitate. If some precipitate remains with the paper, wash it into the dish with a few sharp spurts

* The appearance of a white precipitate (BiOCl , $\text{Sb}_4\text{O}_5\text{Cl}_2$) due to hydrolysis will not interfere with metathesis by H_2S .

† This may require a slow stream of gas for 15 minutes with constant shaking of the flask. The metathesis is more rapid if the solution is kept warm.

of water, using as little as possible. Pour over the precipitate barely enough $(\text{NH}_4)_2\text{Sx}$ to cover it well and warm (not boil) on asbestos with constant stirring for five minutes. Filter, wash the precipitate on the filter with hot water to which some of $(\text{NH}_4)_2\text{Sx}$ has been added, and unite the wash-water with the filtrate (§ 30). Label the filter paper with its precipitate, "Copper Sub-group," and reserve.

Acidify the filtrate with HCl. If no precipitate appears,* As, Sn, and Sb are absent. Proceed with the copper sub-group. But if a colored (lemon-yellow, orange-red, yellow to brown) flocculent precipitate separates, filter, wash with hot water, reject the filtrate and test the precipitate thus:—

1. ARSENIC: Puncture the filter, and wash the precipitate into a small conical flask with sharp spurts of water, using the least possible quantity. Add NH_4OH to alkalinity, then 10-15 cc. $(\text{NH}_4)_2\text{CO}_3$, stopper and shake for five minutes. Filter, wash the precipitate thoroughly, joining the first washing to the filtrate. Label the filter with its precipitate "Sb-Sn," and reserve. Acidify the filtrate with HCl. The formation of a flocculent lemon-yellow precipitate shows arsenic (§ 30).

2. ANTIMONY-TIN: The precipitate labeled "Sb-Sn" is now dissolved in the least possible amount of *aqua regia*, diluted with an equal volume of water, filtered from free sulphur, and tested as detailed in § 30, **tin**, 3 (or 4).

SEPARATION OF THE COPPER SUB-GROUP.

The filter labeled "copper sub-group" is transferred to a small porcelain dish and boiled with HNO_3 . If a residue (yellowish-white or, more commonly black), remains, add an equal volume of water, and filter. Wash the precipitate and label it " Hg ." The filtrate (which should not exceed a volume of 5-10 cc.) is now diluted with an equal volume of alcohol, 1 or 2 cc. of H_2SO_4 added, heated to boiling, then allowed to cool. The separation of a white precipitate (PbSO_4) shows lead (§ 29). Filter.

*The separation of sulphur from the reagent will of course occur. It may be white and very fine, or flocculent and light yellow (sulphur-yellow) to brownish, easily passing through a filter when fine and remaining suspended in the fluid. Be careful not to confuse this separated sulphur with *sulphides of arsenic, antimony and tin*.

3. **COPPER:** Render the filtrate from PbSO_4 (or the solution tested for lead if there was no precipitate) alkaline with NH_4OH . The formation of a deep-blue color shows copper (§ 30). If a white precipitate is formed at the same time, this shows—

4. **BISMUTH:** Filter, wash the precipitate, and confirm as shown in § 30, *Bismuth* 3, 4.

5. **CADMIUM:** The filtrate from bismuth (or the ammoniacal fluid if there was no precipitate) is to be tested for cadmium. If copper was absent, the fluid is clear; saturate it with H_2S (§ 30, *Cadmium*, 2). If the solution is blue, discharge the blue color (§ 30, *Copper*, 2), and then saturate with H_2S . The formation of a yellow precipitate shows cadmium.

6. **IC-MERCURY:** The precipitate labeled “ IIHg ” is dissolved in the least possible amount of *aqua regia*, diluted with an equal volume of water, filtered if not clear, and treated with SnCl_2 . A white to gray or black precipitate shows bivalent mercury (§ 30).

7. **PLATINUM-GOLD:** The contents of the test tube labeled “ Au-Pt ” is now to be tested for the elements indicated. Filter, if not clear, and divide into two portions. Test the first for gold as directed in § 30, *Gold* 2; and the second, for platinum as shown in § 30, *Platinum*, 2.

III.—AMMONIUM-SULPHIDE GROUP

If oxalic acid was found (§ 35 B, 9), it must be removed from the solution labeled “ III ” in order to prevent reduction of salts of the group to the ous-condition. Hence two courses of procedure arise:—

a. Oxalic acid is absent: Proceed as directed in A.

b. Oxalic acid is present: Add 1-2 cc. of **HNO_3** to the solution, evaporate (under the hood) to complete dryness, moisten the residue with **HNO_3** , evaporate, and ignite for a short time at low redness. Dissolve the residue in **HCl** , dilute with a little water, filter if not clear, add 2 cc. of NH_4Cl (§ 33, *Magnesium*, 1), dilute to 30 cc., and proceed as directed in A.

A. Render the solution (brought on from *a* or *b*) alkaline with NH_4OH , boil to expel excess of ammonia (shown by the odor), and

add freshly-prepared $(\text{NH}_4)_2\text{S}$ being careful to avoid much excess. If no precipitate appears, members of this group (Fe, Al, Cr, Co, Ni, Mn, Zn) are absent; proceed to Group IV. If a precipitate is formed, filter rapidly and wash immediately with hot water, to which a few drops of $(\text{NH}_4)_2\text{S}$ have been added, keeping the surface of the precipitate covered with the wash-water. Label the filtrate "IV."

SEPARATION OF THE COBALT-NICKEL SUB-GROUP.

At once treat the precipitate on the filter with special HCl ($1\text{HCl} : 10\text{H}_2\text{O}$). If all dissolves, cobalt and nickel are absent. If a residue remains, it should be black. Label the HCl solution "Iron" and reserve. Examine the black precipitate insoluble in HCl for—

1. COBALT: Test as directed in § 31, *Cobalt*, 2*.

2. NICKEL: If the filtrate from the precipitate by $(\text{NH}_4)_2\text{S}$ is brownish colored, nickel is present (§ 31, *Nickel*, 1). If cobalt was not found as directed above, the borax-bead there obtained is violet to red-brown in color (§ 31, *Nickel*, 2). If cobalt was found, it must be removed before testing the precipitate for nickel. Proceed as directed in § 31, *Nickel*, 3.

SEPARATION OF THE IRON SUB-GROUP.

The filtrate labeled "Iron" is now examined for the remaining members of the group. Boil till the odor of H_2S can no longer be detected, then add a few drops of **HNO_3** , and boil again for 2 minutes.

3. IRON: Pour about 1 cc. of the solution into a test-tube, dilute to 10 cc., and add a drop or two of **KCNS**. A red coloration shows iron (§ 31, *Iron*, 3); if the color is slightly red, report—"A trace of iron."

Since in neutral or alkaline solution iron, aluminum and zinc form nearly insoluble precipitates with PO_4^{---} , if phosphoric acid is present (§ 35, D, 21) it must now be removed. Hence, two courses of procedure arise:—

*For the details of blow-pipe technique see **Martin's Qualitative Analysis with the Blow-pipe**.

a. Phosphoric acid is absent: Proceed as directed below in A.

b. Phosphoric acid is present: Add FeCl_3 to the solution till a drop removed with the glass rod and tested on a porcelain crucible lid gives a brown precipitate ($\text{Fe}(\text{OH})_3$) with a drop of NH_4OH , filter from FePO_4^* , and proceed with the filtrate as directed in A.

A.—SEPARATION OF THE ALUMINUM SUB-GROUP

Concentrate the solution by evaporation to 3–5 cc., *barely neutralize* with $(\text{NH}_4)_2\text{CO}_3$, redissolve any precipitate thus formed with the least possible amount of special HCl ($1\text{HCl}:20\text{H}_2\text{O}$), transfer to a small conical flask, add 10 cc. of BaCO_3 -emulsion, and allow metathesis to go on for several hours, giving the contents of the flask a thorough shaking, meanwhile, about every 15 minutes. This treatment precipitates iron, aluminum and chromium as *ic*-hydroxides, while the chlorides of manganese and zinc are not affected by BaCO_3 ($=\text{Ba}(\text{OH})_2$ from hydrolysis).

Filter and wash with hot water, adding the first wash-water to the filtrate. Label the filtrate “Mn-Zn” and reserve. The precipitate is now to be tested for Al and Cr.

a. Not more than a trace of iron and no H_3PO_4 were found: Dissolve a small portion of the precipitate in HCl , add H_2SO_4 till it occasions no more precipitation (BaSO_4), heat to boiling and filter, rejecting the precipitate.

4. ALUMINUM: Treat 2 cc. of the filtrate with NH_4OH , adding it from a dropping tube held so as to deliver the reagent gently at the surface of the fluid-assay. A gelatinous white precipitate forming a zone at the junction of the two liquids shows aluminum (§ 31, *Aluminum*, 1, 2).

Test the remainder of the filtrate for chromium as directed in *b*, 5 II.

b. Iron or H_3PO_4 was found: Fuse a portion of the BaCO_3 -precipitate with fusing mixture ($1\text{Na}_2\text{CO}_3:1\text{KNO}_3$) in the platinum cup. Extract the melt with a little hot water, filter if not clear, and acidify the filtrate with $\text{HC}_2\text{H}_3\text{O}_2$.

*The phosphates of this group, except that of iron, are soluble in dilute HCl . Hence, all the H_3PO_4 is precipitated as the iron salt.

5. CHROMIUM: Test this filtrate for chromium as directed in § 31, *Chromium*, 3.

Chromium II: The filtrate brought on from 4 may be tested for Cr by treating it with NH_4OH to excess, filtering off the precipitated $\text{Al}(\text{OH})_3$, and then adding $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

Aluminum II: Transfer another portion of the BaCO_3 -precipitate to a small porcelain dish, add 1 g. Na_2CO_3 crystals and 0.5 $\text{Ba}(\text{OH})_2$ crystals, cover with 10 cc. of water and boil 5 minutes replacing the water as it evaporates. Filter, reject the precipitate, acidify the filtrate with HCl , and add NH_4OH to the solution as directed above in 4.

The filtrate labeled 'Mn-Zn' is now to be examined for the elements indicated.

6. ZINC: Acidify 2 cc. of this solution with $\text{HC}_2\text{H}_3\text{O}_2$, and pass H_2S . A white precipitate shows zinc (§ 31, *Zinc*, 1).

7. MANGANESE: Evaporate the remainder of the filtrate nearly to dryness (1 cc. or less) and test as directed in § 31, *Manganese* 2, or 3.

IV.—AMMONIUM-CARBONATE GROUP

If the filtrate from $(\text{NH}_4)_2\text{S}$ labeled 'IV' is colored brown (from nickel), acidify it with $\text{HC}_2\text{H}_3\text{O}_2$ and boil for 5 minutes. Filter, and concentrate to 20-30 cc. in case the volume is greater than that. Cool, render alkaline with NH_4OH , boil, and add to the solution while boiling $(\text{NH}_4)_2\text{CO}_3$ in excess. If no precipitate forms, members of this group (Ba, Sr, Ca) are absent; proceed to Group V. If a precipitate forms, filter, wash thoroughly, add the first wash-water to the filtrate and label it 'V'. Examine the precipitate for barium, strontium and calcium.

Dissolve the precipitate on the filter in the least possible amount of acetic acid*, pouring the same portion (after passing through the filter) over the precipitate so long as it will effect any solution which

*Barium chromate is slightly soluble in $\text{HC}_2\text{H}_3\text{O}_2$. Since Ba is removed from the solution of Ca and Sr as the chromate, an excess of $\text{HC}_2\text{H}_3\text{O}_2$ is to be avoided; otherwise, the separation of barium will not be complete and confusion will ensue when Sr and Ca are tested for.

may be known by the occurrence of effervescence while the liquid is in contact with the solid. The precipitate should be wholly soluble in acetic acid.

1. **BARIUM:** Treat 2 cc. of the acetic acid solution with K_2CrO_4 . If no precipitate is formed, barium is absent. Examine the rest of the solution for strontium and calcium. If a yellow precipitate is formed, barium is present. Add the reagent to the rest of the solution, shake, and filter. Label the filtrate "Sr-Ca" and reserve. Wash the precipitate, and test it further as directed in § 32, *Barium*, 2.

2. **STRONTIUM:** The filtrate labeled "Sr-Ca" (or the solution brought on, if Ba was absent) is now examined for the elements indicated. Make it alkaline with NH_4OH , then add $(NH_4)_2CO_3$. If no precipitate appears, strontium and calcium are both absent. If a precipitate is formed, filter, reject the filtrate, and wash the precipitate till it is entirely white in color. Dissolve it on the filter in the least possible amount of HCl , and divide into two portions. To the first, add $CaSO_4$, heat to boiling, and let stand 10 minutes. If no precipitate appears, strontium is absent. If a white precipitate is formed, strontium is indicated (§ 32, *Strontium*, 2.)

3. **CALCIUM:** If strontium was not found, test the second portion of the HCl -solution at once for calcium *as indicated below after the removal of strontium*. But if strontium is present, it must now be removed. Add K_2SO_4 in excess, boil, filter, rejecting the precipitate, render the filtrate alkaline with NH_4OH , and then add $(NH_4)_2C_2O_4$. A white precipitate shows calcium (§ 32, *Calcium*, 1).

V.—ALKALI-METAL GROUP

Concentrate the filtrate labeled "V" to about 15 cc., put 5 cc. into a test-tube labeled "Mg," and evaporate the remainder to dryness in the hood and ignite the residue so long as white fumes (NH_4Cl) are given off. Dissolve the residue in 5 cc. of water, and filter if not clear, and test this solution for Li, Na, K.

1. **MAGNESIUM:** Test the contents of the test tube marked "Mg" for that element by the method indicated in § 33, *Magnesium*, 1.

2. LITHIUM-SODIUM-POTASSIUM: Test the water solution reserved above for the elements indicated as directed in § 33.

3. AMMONIUM: Transfer the remainder water solution used for the alkali metals to a beaker, treat with 5 cc. of NaOH, cover with a glass plate to the lower side of which you have caused a strip of wet red litmus paper to adhere, and warm gently (do not allow the fluid to boil). Ammonia is shown by the color of the paper changing to blue (§ 33, *Ammonium*, 1).

CHAPTER VIII

PRACTICAL EXERCISES

Having mastered the first five chapters, the student is now prepared to proceed with a consecutive analysis by the directions set forth in Chapters VI–VII.

TWO CASES ARISE: (i) *The substance is a metal.*—Begin at § 36, i, and proceed consecutively. If but one basic ion is found, the metal is elemental; if two or more are found, it is an alloy.

(ii). *The substance is not metallic.*—Begin at § 34 and determine the acid, proceeding systematically as there directed. In case of a mixture, more than one acid may be present. If no acid is found, the “salt” is an oxide (or hydroxide). Then pass to § 36, ii, and, proceeding consecutively, determine the basic ion (or ions). If but one basic ion and one acid ion are found, the salt is readily named; e. g., K^+ and Cl^- , = KCl . If several basic ions are found with one acidic ion, all are salts of the same acid; e. g., Ca^{++} , Cu^{++} , Ag^+ , and NO_3^- , = $Ca(NO_3)_2$, $Cu(NO_3)_2$, $AgNO_3$. But if several acidic ions and several basic ions are found, it is impossible to know their collocation in the mixture. Simply report—The following metals **, **, **, and acids **, **, were found; e. g., Cd^{++} , Ni^{++} , Zn^{++} ; SO_4^{--} , Cl^- , being determined: “The following metals—Cd, Ni, Zn, and the acids— H_2SO_4 and HCl were found.”

Omit no step of the systematic scheme. Write out all reactions involved. Endeavor to follow with “the mental eye” the changes from first to last. And, as soon as possible, fix the whole scheme of analysis in your memory. This will save you much time and add greatly to your enjoyment of the work.

EXERCISES

1. Weigh $AgNO_3$ 0.2 g., $HgNO_3$ 0.2 g., $Cu(NO_3)_2$ 0.2 g., $Co(NO_3)_2$ 0.2 g., and $Ba(NO_3)_2$ 0.2 g. Mix by pouring from one paper to another, pulverize, and again mix thoroughly. Analyze.

2. Weigh CdCl_2 0.2 g., FeCl_3 0.2 g., MnCl_2 0.2 g., CaCl_2 0.2 g., and NH_4Cl 0.2 g. Mix, pulverize, remix, analyze.

3. Weigh $\text{Pb}(\text{NO}_3)_2$ 0.2 g., $\text{Ni}(\text{NO}_3)_2$ 0.2 g., $\text{Sr}(\text{NO}_3)_2$ 0.2 g., and KNO_3 0.2 g. Prepare as shown above, and analyze.

4. Weigh HgCl_2 0.2 g., MgCl_2 0.4 g., NaCl 0.2 g., and LiCl 0.1 g. (since this salt is very hygroscopic, it may be in the laboratory in water-solution only; if so, pulverize the other salts and then add 2 or 3 drops of the saturated solution of LiCl to the mixture). Prepare and analyze.

5. Weigh CdSO_4 0.2 g., $\text{Al}_2(\text{SO}_4)_3$ 0.4 g., K_2CrO_4 0.2 g., and ZnSO_4 0.2 g. Prepare and analyze.

6. Weigh FeSO_4 0.2 g., MnSO_4 0.3 g., ZnSO_4 0.3 g., and $(\text{NH}_4)_2\text{SO}_4$ 0.2 g. Prepare and analyze.

7. Weigh AgNO_3 0.1 g., $\text{Cu}(\text{NO}_3)_2$ 0.2 g., $\text{Bi}(\text{NO}_3)_3$ (if this salt is not available, dissolve 0.1 g of the metal in hot concentrated nitric acid, and add this solution to the solution of the other salts. Read § 31, BISMUTH). Prepare and analyze.

8. Weigh As_2O_3 0.2 g., and SnCl_2 0.3 g. Prepare and analyze.

9. Weigh As_2O_3 0.2 g., pulverize it, dissolve it in 2-3 cc. of hot concentrated HCl , add 0.3 g. of $\text{KSbC}_4\text{H}_2\text{O}_6$ dissolved in 5 cc. of hot water, and analyze for *basic ions only*.

10. Weigh As_2O_3 0.2 g., $\text{KSbC}_4\text{H}_2\text{O}_6$ 0.3 g., SnCl_2 0.3 g., and analyze for *basic ions only*.

11. Weigh $\text{KC}_2\text{H}_3\text{O}_2$ 0.5 g., $\text{KSbC}_4\text{H}_2\text{O}_6$ 0.5 g. Full analysis.

12. Weigh $\text{H}_2\text{C}_2\text{O}_4$ 0.5 g., $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ 0.5 g., and analyze for *acidic ions only*.

13. Make a full analysis of 2 g. of Na_2SO_3 .

14. Make a full analysis of 1 g. of $\text{Na}_2\text{B}_4\text{O}_7$.

15. Make a full analysis of 1 g. of KI .

16. Weigh KI 0.5 g. and KBr 0.5 g. Complete analysis.

17. Make a complete analysis of 1 g. of $\text{K}_4\text{Fe}(\text{CN})_6$.

18. Make a complete analysis of 1 g. of $\text{K}_3\text{Fe}(\text{CN})_6$.

19. Make a complete analysis of NaCl 1 g., KI 0.5 g., and $\text{K}_3\text{Fe}(\text{CN})_6$ 1 g.

20. Make a complete analysis of 1 g. of CaS .
 21. Weigh MgCO_3 , BaCO_3 , and CaCO_3 , 0.5 g. of each. Complete analysis.
 22. Make a complete analysis of 1 g. of Na_2HPO_4 .
 23. Make a complete analysis of 1 g. of KClO_3 .
 24. Analyze 0.5 CaF_2 for HF only.
 25. Analyze 1 g. of sand for H_2SiO_3 only.
 26. Weigh PbO_2 0.2 g., CuO 0.2 g., MnO_2 0.2 g., BaO 0.1 g. Make a complete analysis (both basic and acidic).
 27. Analyze a five-cent coin.
-

NOTE TO THE TEACHER: The pupil may now be exercised on unknowns until his knowledge and skill are proved.

Since the most common source of discouragement to the pupil is found in impurities, all reagents should be made of pure chemicals; and only pure chemicals should be given out for analysis in the foregoing exercises. No "unknown" should be *unknown* to the instructor.

APPENDIX

REAGENTS

ACID—

ACETIC: glacial acetic (sp. gr. 1·04) 1 part,* water 2 parts.

AQUA REGIA: conc. HCl 3 parts, conc. HNO₃ 1 part.

HYDROCHLORIC, CONCENTRATED: sp. gr. 1·12.

HYDROCHLORIC, CONC. ORDINARY: HCl sp. gr. 1·12 with equal volume of water.

HYDROCHLORIC, DILUTE: conc. HCl 1 part, water 4 parts.

HYDROSULPHURIC (H₂S): generate the gas as needed.

NITRIC, CONCENTRATED: sp. gr. 1·42.

NITRIC, DILUTE: conc. HNO₃ 1 part, water 4 parts.

OXALIC: 1 part, water 10 parts.

PHENOL SULPHONIC: phenol 1 part, conc. H₂SO₄ 4 parts, mix in a small flask, warming it occasionally in hot water till solution occurs.

SULPHURIC, CONCENTRATED: sp. gr. 1·84.

SULPHURIC, DILUTE: conc. H₂SO₄ 1 part, water 4 parts.

TARTARIC: 1 part, water 10 parts.

ALCOHOL: C₂H₅OH or CH₃OH, 90 *per cent.*

AMMONIUM—

ACETATE: glacial acetic acid 1½ parts, NH₄OH (sp. gr. 0·9) 1 part.

CARBONATE: water 10 parts, NH₄OH (sp. gr. 0·9) 1 part, (NH₄)₂CO₃, 2½ parts.

CHLORIDE: water 10 parts, NH₄Cl 1 part.

HYDROXIDE (sp. gr. 0·9): water 2 parts, NH₄OH (sp. gr. 0·96) 1 part.

MOLYBDATE: dissolve 25 g. MoO₃ in 100 cc. water to which 20 cc. NH₄-OH (sp. gr. 0·90) has been added, filter, and add with constant stirring to 250 cc. dil. HNO₃ (conc. HNO₃ 1 part, water 2 parts), stand 48 hours in a warm place, then decant.

OXALATE: (NH₄)₂C₂O₄·2H₂O 1 part, water 40 parts.

SULPHIDE ((NH₄)₂S): *make as needed*—saturate 30 cc. NH₄OH (sp. gr. 0·90) with H₂S, add 20 cc. NH₄OH (sp. gr. 0·90) and 40 cc. water.

SULPHIDE, POLY ((NH₄)₂S_x): saturate the colorless (NH₄)₂S with flowers of sulphur.

*Part means *grams* in case of solids, and *cubic centimeters* for liquids.

BARIUM—

CARBONATE: suspend BaCO_3 1 part, in water 4 parts; use as emulsion.

CHLORIDE: BaCl_2 1 part, water 10 parts.

HYDROXIDE: saturate solution; decant and use the clear portion.

CALCIUM—

CHLORIDE: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 1 part, water 10 parts.

HYDROXIDE: see barium.

SULPHATE: saturated solution.

CARBON BISULPHIDE: CS_2 .**FERRIC CHLORIDE: FeCl_3 1 part, water 10 parts.**

INDIGO: add 1 part of pulverized indigo to 5 parts of fuming H_2SO_4 with constant stirring, keeping the acid cool with cold water around the tube or beaker, cover, let stand 48 hours, then pour into 20 times its volume of water, mix and filter.

IRON: filings.**LEAD ACETATE: $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ 1 part, water 10 parts.****LIME WATER: see calcium hydroxide.****MERCURIC CHLORIDE: HgCl_2 1 part, water 20 parts.****POTASSIUM—**

ACETATE: saturated solution.

CHROMATE: K_2CrO_4 1 part, water 10 parts.

CYANIDE: KCN 1 part, water 20 parts.

FERRICYANIDE: $\text{K}_3\text{Fe}(\text{CN})_6$ 1 part, water 100 parts.

FERROCYANIDE: $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ 1 part, water 20 parts.

IODIDE: KI 1 part, water 20 parts.

SULPHATE: K_2SO_4 1 part, water 10 parts.

SULPHOCYANATE: KCNS 1 part, water 20 parts.

SILVER NITRATE: AgNO_3 1 part, water 20 parts.**SODIUM—**

CARBONATE: Na_2CO_3 1 part, water 7 parts.

HYDROXIDE: NaOH 1 part, water 10 parts.

PHOSPHATE: $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ 1 part, water 10 parts.

STANNOUS CHLORIDE: dissolve 50 g. of tin in hot conc. HCl , add 4 times its volume of water, filter if not clear, and keep an excess of granulated tin in the solution.



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